CLAY MINERALOGY OF SOME PERMIAN SHALES AND LIMESTONES

by

LORIS ELDEN ASMUSSEN

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INTRODUCTION

Purpose of Investigation

The purpose of this investigation was to determine the non-carbonate mineralogy of the two micron and smaller size fraction of the minerals present in the Permian shales and limestones of Riley and Geary counties Kansas. The limestones were further investigated and a heavy and light mineral analysis was made. This investigation was a continuation of McPherron's (1956) and Watkins's (1957) investigation, and an attempt was made to correlate the clay mineral results of their theses with this investigation.

An attempt was also made to make a correlation between the clay minerals, chert composition, and physical appearance of the shales and limestones investigated. Previously some relationship had been noticed between montmorillonite and chert bearing limestones, and this in turn appeared to be related to the volcanic ash content. If this relation could be proven it would explain the origin of the large amounts of chert found in the limestones of eastern Kansas.

Methods Used

Two methods were used primarily in this investigation, X-ray diffraction analysis and differential thermal analysis. These methods were supplemented by staining, optical methods, and thermal dehydration methods. By using a combination of these a relatively accurate identification of the mineralogy of the Permian shales and limestones was obtained in this investigation.

REVIEW OF LITERATURE

Shale

Shale is a fine grained detrital sedimentary rock produced by rock weathering, transportation, and deposition. The size variation of these weathered particles being from 1/16 mm. to 1/256 mm. with clay size particles being less than 1/256 mm. Shale is composed of laminated (or fissile) claystone and siltstone. Ingram (1953) defined claystone as a massive rock in which clay predominates over silt (whereas siltstone is used for massive rocks in which silt exceeds clay). The term mudstone is used when the proportions of claystone and siltstone are unknown. Twenhofel used the term mudstone to include clay, silt, siltstone, claystone, shale and argillite, which is more inclusive than Ingram's definition.

Shales can be classified by their detrital mineral composition or by their origin. Krynine (1948) classified them by detrital minerals present into: quartzose shale, micaceous shale, chloritic shale, and kaolinitic or feldspathic shale. Pettijohn (1957) classified shales by origin into two major groups, residual and transported.

Limestone

The term limestone is applied to sedimentary rocks in which the carbonate fraction exceeds the noncarbonate fraction. Usually this carbonate fraction is composed primarily of calcite. Dolomites are limestones containing more than 50 per cent carbonate, of which more than half is dolomite. There is still a great deal of disagreement on the definitions, and the above mentioned definitions are an adaptation of Rodgers (1954) survey. Further information on classification, definition, chemical composition, and deposition can be obtained from (Pettijohn, 1957; Watkins, 1957).

The depositional environment of limestones is one of great variety. Sloss and Krumbein (1951) classified limestones into three categories on the basis of their depositional environment: (1) platform, (2) basin, and (3) geosynclinal. These environments in turn regulate the chemical composition of limestone to a certain extent. Limestones are primarily calcite, therefore, high in CaO and CO_2. Magnesium oxide is also high in the dolomitic varieties. If magnesium oxide exceeds one to two per cent there is a possibility that the mineral dolomite is present (Pettijohn, 1957). Dolomite is either deposited by replacement, (Pettijohn, 1957) p. 421, or by primary deposition. If silica is present in excessive amounts it is an indication of non-carbonate detritus or the presence of authigenic chert (Pettijohn, 1957) p. 383. Pettijohn (1957) pp. 393-411, and Twenhofel (1950) p. 356, classified limestones according to the method of accumulation of calcareous material.

Clay Mineralogy

The clay mineral concept as known today did not come into existence until after 1920. Before this time ideas such as these were prevalent: all clays were kaolinite with varying amounts of other materials as impurities; all essential components of clay minerals were present as a colloid complex; and clays were developed from two essential components, clayite and pelinite. Numerous ideas such as these were held up until the present day clay mineral concept came into existence. Grim (1953) p. 18, said,

> "According to the clay mineral concept clays generally are essentially composed of extremely small crystalline particles of one or more members of a small group of minerals which have come to be known as the clay minerals. The clay minerals are essentially hydrous aluminum silicates, with magnesium or iron proxying wholly or in part for the aluminum in some minerals and with alkalies or alkaline earths present as essential constituents in some of them".

While many people were responsible for developing this concept special

attention should be called to these: Hadding and Rhinne working with X-ray diffraction, Ross and Shannon using petrographic methods, and Marshall working with optical properties.

The work of Hadding and Rhinne in 1920 is especially important because it was the first work in X-ray diffraction of clay minerals and established their crystalline structure. By this method it is also possible to identify clay minerals.

Clay may occur as residual clay or as transported clay (Ries, 1927) pp. 1-10. The residual clays are formed on the weathered surface of rocks by at least three methods: decomposition of silicate minerals of the rock, the product having all the properties of clay; solution of a carbonate rock containing insoluble clayey impurities, which are left behind as an insoluble residue; and the disintegration, accompanied possibly by some alteration of shales. Other methods of forming residual clays are by hydrothermal solutions, and alteration by meteoric waters. Residual clays are found in all portions of the United States, but in larger quantities in areas east of the Mississippi River and south of the southern margin of the ice sheet.

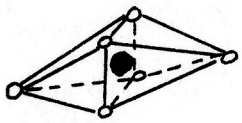
Transported clays or sedimentary clays are those that are moved from their area of formation to an area of deposition. Their mode of transportation and deposition in many cases gives them a classification name: marine clays, estuarine clays, swamp and lake clays, flood-plain and terrace clays, delta clays, eolian clays, and chemical clays.

Clay minerals are classified according to structure and composition of the various minerals as presented by Grim (1953) p. 27. This classification will probably undergo a great many changes in the future, due primarily to the fast changing ideas and concepts of clay minerals. Grim's major subdivisions are amorphous clay minerals and crystalline clays, with very little information

being available on the amorphous clays. The crystalline group is then divided into expanding and non-expanding types, but this eventually will probably be changed due to gradation between the two. The division into elongate and equidimensional types of clay minerals will probably also be changed for the same reason.

The nomenclature of clay minerals used by Grim is adapted to this classification. The only amorphous clay known at present is allophane. It has been suggested that it is really a crystalline variety, but positive proof is lacking. Most of the crystalline clays are found under the major groups: kaolinite, illite, halloysite, montmorillonite, vermiculite, chlorite, and the chain silicate clays. Each major group of crystalline clays has three or four members except in two cases and more members are being found for many of the groups.

The structure of clay is based on two major units. One unit consists of two sheets of closely packed oxygens or hydroxyls in which aluminum, iron, or magnesium atoms are embedded in octahedral coordinations, so that they are equidistant from six oxygens or hydroxyls (Pauling, 1930) pp. 123-129. When aluminum is present, only two-thirds of the possible octahedral positions are

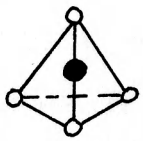


O -Oxygen or hydroxyl

● -Mg, Fe, or Al

filled to balance the structure giving it the name heptaphyllites, or dioctahedral. When magnesium or iron is present all the octahedral positions can be filled giving it the name octaphyllite or trioctahedral. The second unit in the clay structure is built of silica tetrahedrons. In each tetrahedron a silica atom is equidistant from four oxygens or hydroxyls arranged in the form of a tetrahedron with a silica atom at the center. These are then arranged in a hexagonal network with the tips pointing in the same direction and the base in the same plane (Pauling, 1930) pp. 123-129. Each clay mineral has a dif-

ferent structure and arrangement of these octahedrons and tetrahedrons. Even



O-Oxygen

●-Silica

a single clay can undergo some changes in its structure and this structure is affected by the water and exchange ions present. The water does not get into the octahedrons and tetrahedrons, but it may separate them.

X-ray diffraction is one of the important methods of clay identification. There are two types of sample orientation: random and oriented. Oriented samples give the distances in angstroms between the basal sections (001, 002, etc.). In non-orientated samples the X-ray gives reflections from all planes as well as basal sections. The chain silicate clays are elongate and do not orient parallel to the basal pinacoids (Grim, 1953) p. 99. Randon orientation is obtained when samples are in the powder form, and the orientated samples are obtained when the sample is put on a slide in a liquid suspension which is allowed to dry producing a definite orientation parallel to the basal pinacoid. From orientated samples it is a great deal easier to get basal spacings due to the orientation parallel to the basal pinacoids when the sample dries on the slide.

All clays exhibit a property called ion exchange. This is probably one of the most important properties of clay. It affects a great many fields; Agronomy, through ion exchange between clays and plants; Geology in that it affects weathering and also indicates the environment of certain sediments; in oceanography the concentration of sodium in sea water is due partly to the ability of clay to fix potassium and, therefore, increasing the ion concentration of sodium; in Art it affects industries such as ceramics, brick making, and pottery; and it also affects construction by changing plasticity, compaction, and shrinkage properties of soils.

Ions are of two types: cations (Ca, Mg, H, K, NH_4, Na) and anions (SO_4, Cl, PO_4, NO_3). At the present time, a great deal more is known about the cation exchange of clays than is known about their anion exchange. The ions are held by metallic (electron clouds), ionic (coulombic forces), and covalent (shared electrons) forces. The types of exchange that in turn affects the amount of exchange are: substitution in the lattice; broken bonds, which increases with decrease in particle size; and hydrogen bonding, which is due to exposed hydroxyls. Anion exchange is similar to cation exchange except for the charge. It is also possible to have exchange by PO_4 anion substitution in place of the silica tetrahedrons in the lattice. The factor that affects ion or base exchange the most is the amount of water present in the clay mineral structures as interlayer water. Clays such as montmorillonite, halloysite, and vermiculite, have high base exchange because part of the water can be replaced by the ions. Clays such as kaolinite, chlorite, and illite have low exchange because they have little substitution in the lattice and, therefore, only broken bonds or exposed hydroxyls are available as exchange points.

The water in the clay mineral system is of four types: pore and film water, interlayer water, chain water, and OH water. All types are quite easy to remove, with interlayer and OH water the only ones to require heating to over one hundred degrees centigrade. The OH water is probably arranged in a crystalline form which is similar to that of ice. This produces a film that acts as a solid around the crystals of the clay and as the interlayer film between silica tetrahedrons and aluminum octahedrons. The orientation of these water molecules produces a reaction called the heat of wetting (Grim, 1953) p. 183. The indication of this reaction being a slight rise in temperature of the clay when water is added to dehydrated clays indicating a molecular movement to form a crystalline arrangement.

The presence of water is indicated by several means. The first and simplest is by heating and weighing the sample as it is heated to determine the loss water, this is called thermal dehydration. Another means is by differential thermal analysis, which is the measurement of the difference of temperature between a test sample and a definite known substance in which very little or no reaction takes place. In differential thermal analysis a definite pattern for loss of weight is known. The general order being loss of interlayer water, loss of OH water, loss of hydrogen, loss of organic material, and the loss of CO_2 (Jackson, 1950) p. 202. All of these except the organic matter produce definite endothermic reactions up to a temperature of about 800 degrees centigrade. The reactions from 800° C. on up are usually exothermic, but in certain cases may be endothermic when heat is taken up.

The exothermic reactions are produced by the formation of the high temperature minerals. Each clay has a different set of high temperature minerals and each of these are produced at definite temperatures. Some of these minerals are spinel, alpha aluminum oxide, beta quartz, cristobalite, enstatite, cordierite, and mullite (Grim, 1953) p. 211. These minerals are important to the ceramic industry in which high temperatures are produced in the processing of the products. These high temperature minerals can be identified by the use of X-ray, microscope, and partially by differential thermal analysis.

The things that affect differential thermal analysis and give endothermic and exothermic peaks are: water, impurities, oxidation of iron and magnesium, thermo-couples arrangement and size, and the size of the sample. It is very important to have the thermo-couples of equal size and centrally located in the sample. A drifting effect will be produced if these qualifications are not observed. In some cases this drift effect can be very pronounced (Jackson, 1950) pp. 205-207.

The above mentioned methods of clay analysis and identification are affected to a great extent by the purity of the clay. Many clays are a mixture; in fact it is very rarely that a pure clay is found. Clay mineral mixtures are of three types: mechanical, regular interlayered, and random interlayered. The first is the easiest to identify, produce, and work with. In a mechanical mixture, there must be at least ten per cent of the minor constituent to be identifiable in most cases. Regular interlayered clay minerals may be common. The best example that is known at the present time is chlorite. It has the silica tetrahedrons, aluminum octahedrons, and brucite layers in a definite pattern. The last, or random interlayered type, is very common in natural clays. In this type there is no regular sequence of the different layers.

Organic compounds may have a large affect on clay minerals when present in the clay mineral structure. In soils, plants derive part of their nutrition from organic compounds in the clay mineral structure. Organic compounds in the clay may be a possible explanation of migration, collection, and origin of petroleum. These organic ions are held by Van der Waals forces, coulombic forces, and hydrogen bonds (Grim, 1953) pp. 250-255. The Van der Waals forces do not require a charge on the clay particles for the bonding. If the organic molecule is adsorbed on the basal plane it produces a definite c-axis shift. It is by this means that montmorillonite is identified in X-ray analysis; but to have adsorption of the basal plane interlayer water is required. This ionic adsorption takes place by the means previously discussed in ion or cation exchange. This organic compound adsorption may also be used in determination of surface area, in explaining peaks in differential thermal analysis, for the estimation of exchange capacity, and in stain testing of clays (Grim, 1953).

One of the oldest and a still widely used methods of clay mineral identification is the optical method. Work with the microscope is done on three

types of clay samples: dried samples, oriented aggregates, and thin section. Thin sections for clay minerals are very hard to prepare and expensive. One of the draw backs to optical methods is the reaction of the clay with the organic liquids used for immersion in many cases. The hardest clays to work with optically are montmorillonite and halloysite. The other clay minerals have relatively stable optical properties.

Other methods of clay mineral identification are infrared spectra, solubility, decomposition by electrodialysis, and measurement of surface area. These methods of identification are little used and in many cases lack accuracy. Probably the only one that will ever be used to any extent is the infrared spectra, which produce curves similar to X-ray curves due to the constant vibration of the molecules.

Clay minerals will be used more and more in the future for determining environmental differences during their deposition. Weaver (1956) stated that illite-montmorillonite and chlorite-montmorillonite rather than pure illite and chlorite clays are formed by marine diagenesis. It is the author's opinion that vermiculite-chlorite is also indicative of marine diagenesis.

In most cases the clays have sustained some weathering before deposition which produces a significant change in them. Harrison and Murray stated at the 1957 Clay Mineral Conference that montmorillonite often formed at the expense of iron rich chlorite. The montmorillonite is usually not pure and is in the random interlayer form. They also determined that montmorillonite forms at the expense of illite. The montmorillonite and illite forms a segregated mixed-layer species in which zones of varying densities of montmorillonite layers are interspersed throughout the illite layers. These islands within the illite are reflected in the diffraction patterns by assymetry on the low-angle side of the (001) peak of illite, assymetry on the high-angle side of the (003) peak, and broadening of the (002) peak.

Kaolinite is not as greatly affected by weathering as the other clays, and it is usually not found in very large amounts in marine sediments. Grim (1953) seemed certain that chloritic mica and illite tend to form during marine diagenesis from other clays. The clays may also be due to land derived muds, which absorb potassium and magnesium from sea water.

In the past a great many investigators believed that montmorillonite was absent from marine sediments older than Mesozoic. Grim (1953) explained the absence by compaction, dehydration, and absorption of potassium and magnesium during the course of time. But investigations made by Swineford (1955), Hartig (1954), McPherron (1956), and Watkins (1957) have shown the presence of montmorillonite in the shales and limestones in the north-eastern part of Kansas. Hartig (1954) found that montmorillonite occurred above and below the chert bearing limestones in the Manhattan area. This was further substantiated by McPherron and Watkins. Wilbur (1956) found volcanic shards in the limestone parts of the chert bearing limestone. These in turn, seem to be related to the montmorillonite found just above or below these limestones.

Weaver (1956) stated that the mixed-layer clays are either formed by diagenesis in the basin of deposition or by weathering in the source area. However, it is believed that originally a large part of the mixed-layer illite-montmorillonite and chlorite-montmorillonite clays are formed by marine diagenesis, whereas mixed layer chlorite-vermiculite clays, primarily because of their relatively large grain size, are usually considered to have been formed by weathering.

X-ray identification of mixed layer clay minerals is based on the average value resulting from the simultaneous scattering by both types of layers. The position depends upon the relative amounts of the two layers (001/001).

AREA OF INVESTIGATION AND FIELD PROCEDURE

The limestones and shales used in this investigation were collected in the immediate Manhattan area. They are all members and formations of the Council Grove Group of Permian age. The samples were collected in road cuts, stream beds, and surface exposures.

All the sampling was of the "spot" type. Krumbein and Pettijohn (1938) defined this as sampling at isolated spots at particular points within an outcrop. This is the best method of checking the clay mineral composition within a single small rock unit. Care must be taken to make sure that weathered material is not incorporated in the sample. The weathering of shales and limestones may change the clay mineral content. Each sample was placed in sample boxes which were then labeled as to location, sample number, stratigraphic horizon, and a short lithologic description was written.

LABORATORY PROCEDURE

Preparation of Clay-size Materials

Limestones. The first consideration in preparation of the limestone samples for clay mineral analysis was given to the possible loss of the clay minerals when the sample was treated for the removal of carbonates. Chlorites and certain types of montmorillonite are affected or in some cases destroyed by hydrochloric acid which was used to remove the carbonates (Grim, 1953) p. 359. Because of the chance of destroying these clays no acid treatment was used on the limestones. It should be taken into consideration that if the carbonates are not removed they may affect the orientation of the clay size particles on the slides. A comparison was made; and it was noted that there

EXPLANATION OF PLATE I

Map of the Geary, Pottawatomie, Riley, and Wabaunsee Counties showing locations of sample sites.

PLATE I

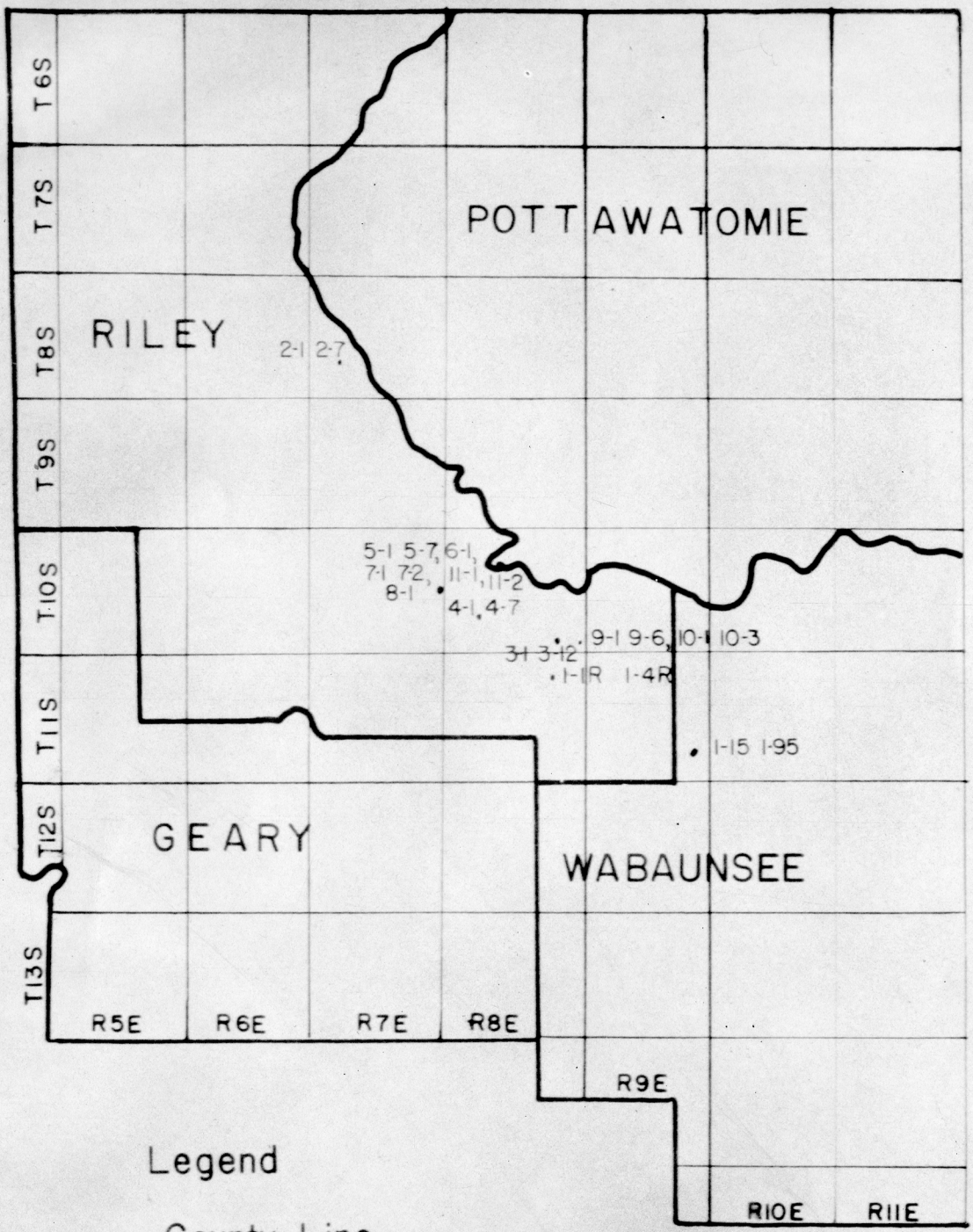

T6S
T7S
T8S
T9S
T10S
T11S
T12S
T13S
R5E
R6E
R7E
R8E
R9E
R10E
R11E
POTTAWATOMIE
RILEY
GEARY
WABAUNSEE
2-1 2-7
5-1 5-7, 6-1,
7-1 7-2, 11-1, 11-2
8-1
4-1, 4-7
9-1 9-6, 10-1 10-3
3-1 3-12
1-1R 1-4R
1-15 1-95
Legend
County Line
Township Line
Sample Location Number
Scale
0 6 12miles

Table 1. Location of sampled units.

Sample Number	Member or Formation'	System	Land Description	County
1-1R	Blue Rapids'	Permian	Sec. 4, T11S, R8E	Riley
1-2R	Blue Rapids'	Permian	Sec. 4, T11S, R8E	Riley
1-3R	Blue Rapids'	Permian	Sec. 4, T11S, R8E	Riley
1-4R	Blue Rapids'	Permian	Sec. 4, T11S, R8E	Riley
2-1	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-2	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-3	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-4	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-5	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-6	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
2-7	Blue Rapids'	Permian	Sec. 19, T 8S, R7E	Riley
3-1	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-2	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-3	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-4	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-5	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-6	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-7	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-8	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-9	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-10	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-11	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
3-12	Eskridge'	Permian	Sec. 32, T10S, R8E	Riley
4-1	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-2	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-3	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-4	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-5	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-6	Neva	Permian	Sec. 6, T10S, R8E	Riley
4-7	Neva	Permian	Sec. 6, T10S, R8E	Riley
5-1	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-2	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-3	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-4	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-5	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-6	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
5-7	Johnson'	Permian	Sec. 13, T10S, R7E	Riley
6-1	Glenrock	Permian	Sec. 13, T10S, R7E	Riley

Table 1. (concl.)

Sample Number	Member or Formation'	System	Land Description	County
7-1	Bennett	Permian	Sec. 13, T10S, R7E	Riley
7-2	Bennett	Permian	Sec. 13, T10S, R7E	Riley
8-1	Howe	Permian	Sec. 13, T10S, R7E	Riley
9-1	Roca'	Permian	Sec. 32, T10S, R8E	Riley
9-2	Roca'	Permian	Sec. 32, T10S, R8E	Riley
9-3	Roca'	Permian	Sec. 32, T10S, R8E	Riley
9-4	Roca'	Permian	Sec. 32, T10S, R8E	Riley
9-5	Roca'	Permian	Sec. 32, T10S, R8E	Riley
9-6	Roca'	Permian	Sec. 32, T10S, R8E	Riley
10-1	Burr	Permian	Sec. 32, T10S, R8E	Riley
10-2	Burr	Permian	Sec. 32, T10S, R8E	Riley
10-3	Burr	Permian	Sec. 32, T10S, R8E	Riley
11-1	Salem Point'	Permian	Sec. 13, T10S, R8E	Riley
11-2	Salem Point'	Permian	Sec. 13, T10S, R8E	Riley

EXPLANATION OF PLATE II

Plate II shows a stratigraphic column of the rocks sampled. This column shows the approximate thickness of the limestones and shales in the Manhattan area. Some shales have thin limestones lenses in them. The sample numbers are indicated along the side of the column.

PLATE II

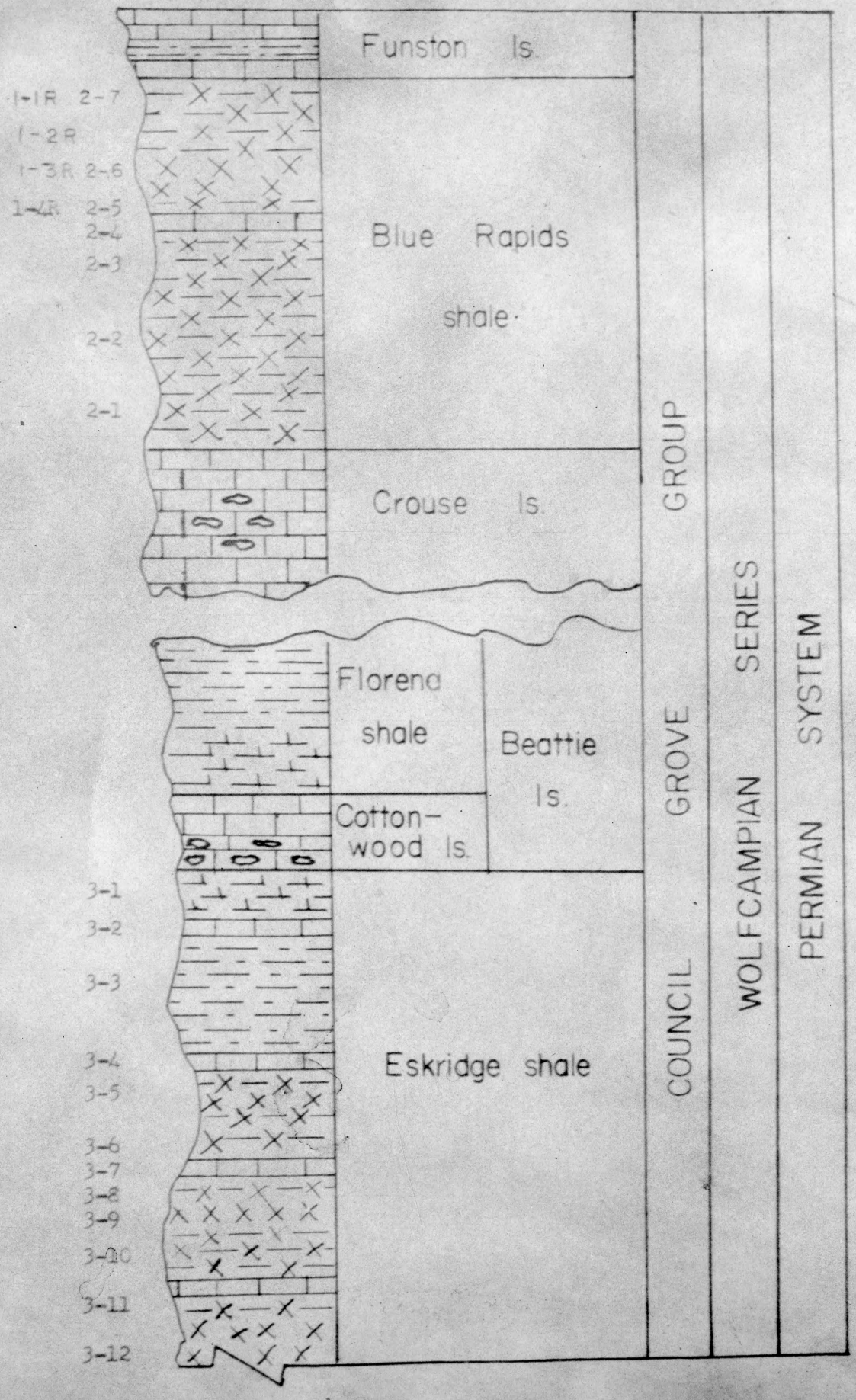

Funston ls.
1-1R 2-7
1-2R
1-3R 2-6
1-4R 2-5
2-4
2-3
Blue Rapids
shale
2-2
2-1
Crouse ls.
Florena
shale
Beattie
ls.
Cotton-
wood ls.
3-1
3-2
3-3
3-4
3-5
Eskridge shale
3-6
3-7
3-8
3-9
3-10
3-11
3-12
COUNCIL GROVE GROUP
WOLFCAMPIAN SERIES
PERMIAN SYSTEM

PLATE II (cont.)

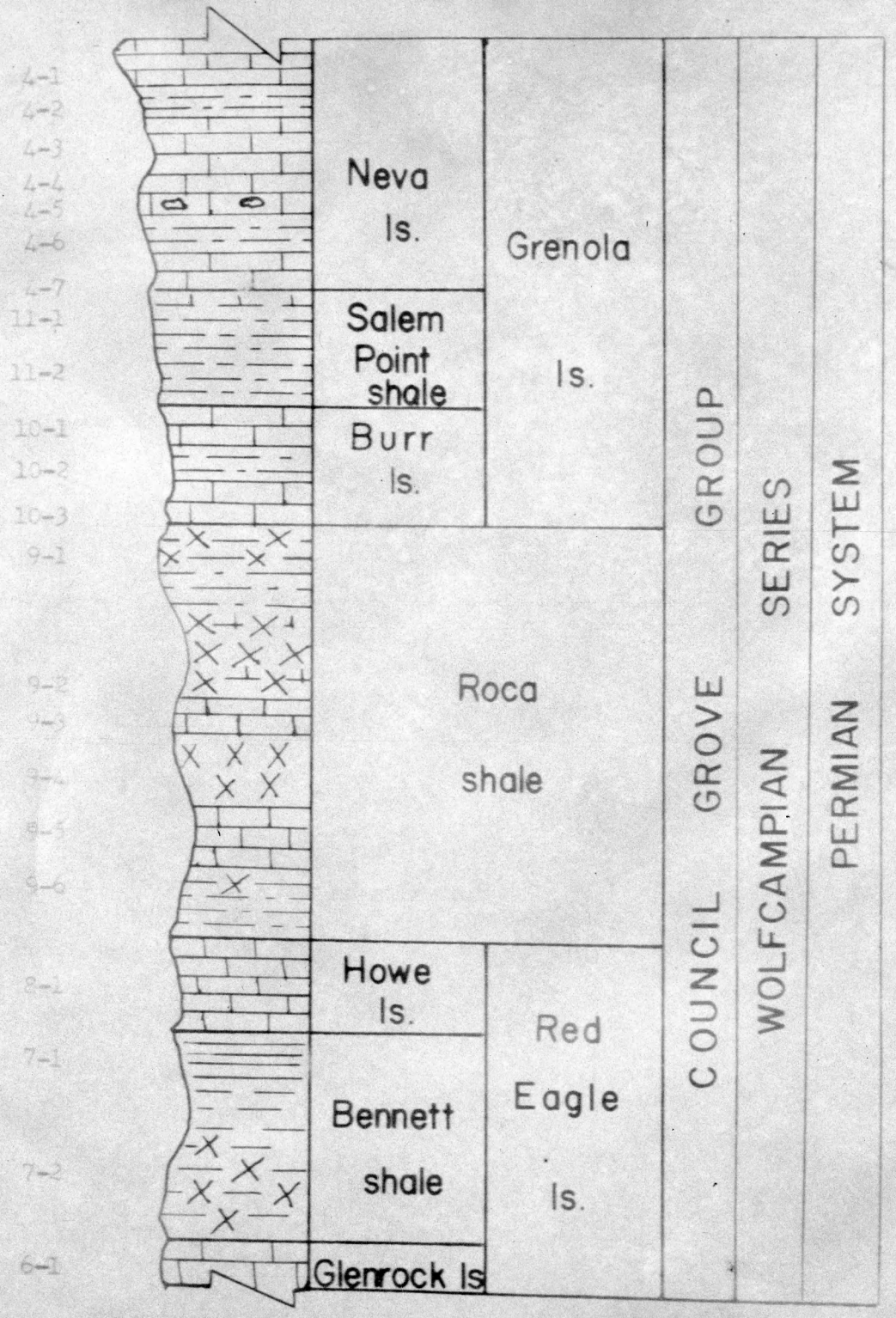
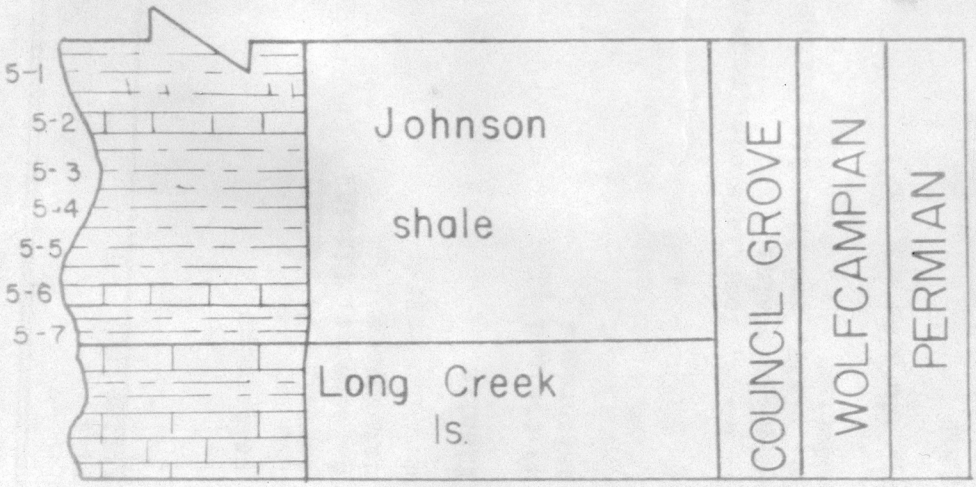
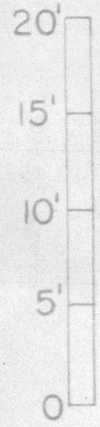


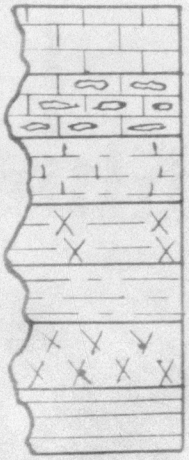
PLATE II (cont.)



Scale
one inch equals
ten feet



Legend



Limestone
Cherty Limestone
Calcareous Shale
Green Shale
Gray or Tan Shale
Red Shale
Black Shale

Table 2. Description of geologic section showing the relationships of the color of unweathered, weathered, and clay size fraction of samples from the Council Grove Group.

Geologic Section		Color Unweathered	Color Weathered	Color Clay Fraction	Lithologic Description
Blue Rapids Shale	25'				
1-1R	Top	Gray	Tan to gray	Light green	Shale, calcareous
1-2R		Black	Gray	Gray	Shale
1-3R		Red	Red to black	Red to brown	Shale, contains Fe staining
1-4R	Middle	Green	Gray to green	Light green	Shale, calcareous, fissile
2-7	Top	Gray to green	Gray	Light green	Shale, calcareous
2-6		Red	Red to brown	Buff	Shale
2-5		Gray to green	Gray	Light green	Shale
2-4		Gray	Gray to tan	Light green	Shale, fissile
2-3		Green	Green to gray	Green	Shale
2-2		Red	Brown	Buff	Shale, Fe stained
2-1		Green	Tan	Olive green	Shale, calcareous
Eskridge Shale	33'				
3-1	Top	Brown	Tan	Light brown	Shale
3-2		Pink to purple	Buff	Buff	Limestone ledge, fossileferous, nodeular
3-3		Gray	Buff	Light gray	Shale, limonite stains
3-4		Gray	Light brown	Light gray	Limestone, platy, and limonite stains
3-5		Olive green	Gray	Light green	Shale, nodeular
3-6		Light brown	Brown	Yellow	Shale
3-7		Gray	Brown	Light green	Limestone, limonite stains
3-8		Tan to green	Buff	Light green	Shale
3-9		Purple	Dark purple	Buff	Shale, platy
3-10		Green to gray	Gray	Green	Shale, limonite stains, local limestone ledges, and fossileferous
3-11		Gray	Tan	Light gray	Limestone, with small shale partings, calcite crystals, and limonite stains
3-12		Red to black	Brown	Brown	Shale, nodeular

Table 2. (cont.)

Geologic Section		Color Unweathered	Color Weathered	Color Clay Fraction	Lithologic Description
Neva Limestone	14'				
4-1	Top	Gray	Buff	Green	Limestone, massive
4-2		Tan to brown	White to tan	Light green	Shale, platy
4-3		Gray	Tan	Tan	Limestone, massive, honeycombed
4-4		Red to brown	Brown	Brown	Marl
4-5		Tan to brown	Light brown	Light tan	Limestone, calcite geodes
4-6		Gray	Brown	Light green	Shale, limonite stains
4-7		Gray	Brown	Light brown	Limestone, fossiferous
Johnson Shale	20'				
5-1	Top	Gray	Light tan to gray	Light green	Shale, calcareous lenses
5-2		Gray	Tan to white	Tan	Limestone, limonite stains
5-3		Brown to gray	Tan	Light green	Shale, fissile, limonite stains
5-4		Brown to gray	Tan	Tan	Mudstone, limonite stains
5-5		Tan	Gray to white	Tan	Shale
5-6		Tan	Tan	Tan to white	Limestone
5-7		Black	Black to tan	Gray	Shale, fissile
Glenrock Limestone	2'				
6-1		White	Gray	Tan to brown	Limestone, massive, fusilinids
Bennett Shale	10'				
7-1	Bottom	Black	Gray	Black	Shale
7-2		Tan to green	Tan	Gray	Shale, fossiliferous

Table 2. (concl.)

Geologic Section		Color Unweathered	Color Weathered	Color Clay Fraction	Lithologic Description
Howe Limestone	4'				
8-1		Tan	Brown	Tan to brown	Limestone, pitted, limonite stains
Roca Shale	18'				
9-1	Top	Green to tan	Tan	Light green	Shale, limonite stains
9-2		Red	Purple	Brown	Shale, nodeular
9-3		Red to green	Gray	Light green	Shale to limestone
9-4		Red	Pink	Brown	Shale, nodeular
9-5		Buff	Light brown	Buff	Limestone, calcite crystals
9-6		Green to tan	Gray to green	Light green	Shale, platy
Burr Limestone	10'				
10-1	Top	Light gray	Tan	Light gray	Limestone
10-2		Gray	Tan	Light gray	Shale, upper fissile
10-3		Tan	Tan	Tan	Limestone, fossileferous
Salem Point Shale	8'				
11-1		Gray	Tan	Tan	Shale, calcareous
11-2		Gray to black	Gray	Light gray	Shale

was a sharpening and decreased intensity of the calcite peaks, complete removal of the chlorite peaks, and a reduction in the intensity of the entire sample in the treated samples. Another problem encountered was the lack of concentration of the clay size fraction.

The general sample procedure was taken from Jackson (1950) with several revisions to meet specific needs. The limestones required special care due to their high carbonate content, and it required larger samples to get a large enough concentration of clay size particles to analyze.

A sample of 150 grams was run through a jaw crusher, then ground with a mortor and pestle. The sample was then put in a Waring Blender along with 300 milliliters of distilled water, 60 milliliters of sodium silicate solution, and agitated for 15 minutes. In some cases it was necessary to add more sodium silicate to prevent flocculation of the sample in the sedimentation tube.

After agitation the sample was screened through a U. S. # 270 (.053 mm.) sieve. The silt and clay fraction was transferred to a sedimentation tube and enough distilled water was added to make a total volume of 1000 milliliters. The tube was then placed in a constant temperature bath at 20 degrees centigrade for 36 hours. Twelve hours for each 10 centimenters of settling distance is required, and 30 centimenters was decanted from the sedimentation tube into a gallon glass jug after 36 hours. The portion left in the bottom of the sedimentation tube was then placed in a Waring Blender, agitated for five minutes, and transferred back to a sedimentation tube with enough distilled water to make a volume of 1000 milliliters. The above procedure for the first separation was followed with the exception that it was allowed to settle only 24 hours due to the different concentration. The sample was then decanted again and placed in the same sample jug, and the silt fraction left in the sedimentation tube was removed.

After the silt removal an aliquot of the clay fraction was saved to make X-ray slides and to the rest 1/10 N. HCl acid was added until the clay fraction flocculated out of the suspension. Water from the top of the sample was then decanted. The sediment was vacuum-filtered in a Buechner funnel using Whatman number 42 filter paper. The sample deposited on the filter paper was then washed several times to remove the acid and soluble salts and then dried. After drying it was then put into a bottle to be used for differential thermal analysis, supercentrifuge separation, and stain tests.

Slides for X-ray analysis were prepared from an aliquot with the sample still in liquid suspension. A sample of this aliquot was put on glass microscope slides (2 inches long) with an eye dropper and allowed to air dry at room temperature. This drying produced a film of clay on the slides with orientation parallel to the basal pinacoid of the clay crystals which results in easier X-ray diffraction analysis.

It was found in X-ray analysis of the limestone that the orientation was not disturbed by the colloidal calcite and quartz, and very little difficulty was encountered using different concentrations of the suspension.

Shales. The sample procedure for the shales was the same as for the limestones except the carbonates were removed by the use of 1/10 N. HCl acid and only 100 grams of the sample was used. It was not necessary to remove the organic matter due to its low concentration and lack of effect on the X-ray diffraction patterns. The organic matter did have a limited effect on the differential thermal analysis and stain testing, and this effect was taken into consideration in the interpretation of the results.

Slide preparation for the X-ray analysis was the same as for the limestones with no concentration difficulties being encountered. After the X-ray analysis it was found that it was not necessary to remove the carbonates, and

they did not disturb the orientation or confuse the interpretation of the X-ray patterns unless they were present in very high concentration.

An additional Buechner funnel separation was required when the carbonates were removed. This separation was required to remove the HCl acid and soluble salts from the sample before it was suspended in the sedimentation tubes. After this washing the sodium silicate was added to prevent flocculation. The rest of the procedure was the same as for the limestones.

Supercentrifuge Size Separation

The separation of the clay fraction (-2 micron) was done with a Sharples laboratory model air-turbine supercentrifuge. Two separations were made resulting in 3-size fractions, 0.2 to 2 microns, .08 to 0.2 micron, and less than .08 micron. The samples of larger size than the size being separated were collected on a cellulose liner of the clarifier bowl. This liner is used to expediate the cleaning of the bowl. Several separations are usually required at each size level with the exception of the .08 micron level. One separation was required at this level in this case due to the lack of .08 micron and smaller size fraction.

The .08 and less micron separation was made first. The supercentrifuge bowl revolves at a rate of 25,000 revolutions per minute. At this speed the rate of flow should be 100 ml/min using the small feed nozzle. To produce the 25,000 r.p.m. an air pressure of 14 to 16 pounds per square inch is required. The desired rate flow is produced by the use of two reservoirs with the height of the surface of the liquid being about 100 to 120 centimeters from the table top to the liquid surface in the lower reservoir.

After the .08 micron and smaller separation, the sample on the cellulose liner was placed in a Waring blender and mixed for five minutes. This sample

was then added to about a gallon of distilled water, poured in the top reservoir, and allowed to flow into the bottom reservoir maintaining a constant water level. The liquid that was caught after going through the centrifuge contained the .08 to 0.2 micron size fraction.

The cellulose liner was removed from the centrifuge, and the sample remaining on it was from 0.2 to 2 microns. The procedure for the separation of the .08 to 0.2 micron was the same as for the 0.2 to 2 microns size fraction. Several separations were required to get complete separation between the .08 to 0.2 micron and .2 and 2 microns size fractions.

The only separations that produced workable samples were the .08 to 0.2 micron and the 0.2 to 2 micron level. When flocculation of the .08 and smaller micron size fraction was attempted by the use of hydrochloric acid there did not seem to be any noticeable precipitation or any noticeable material left in suspension. There seemed to be about equal amounts of .08 to 0.2 micron and 0.2 to 2 micron size fraction. Slides were made of these two size fractions and X-ray analysis was run on them.

X-ray Diffraction Analysis Methods

The X-ray unit is divided into three separate components: water-cooler, North American Philips diffraction unit, and North American Philips Electronic Circuit Panel. The diffraction unit is equipped with both cameras and geiger counter goniometer. The goniometer permits the use of both powder and oriented slides in the clay mineral analysis, but in this case most of the work was done on oriented slides. Slides were exposed to nickel filter copper radiation, using 20 milliamps and 40 kilovolts with a one degree slit system, rate meter scale factor of four or eight, with time constant of four seconds. Scanning speeds of the goniometer used were 1/4 degree two theta per minute or one

degree two theta per minute. The goniometer was run through various angles, but most of the samples were run through a 30 degree to 2 degree two theta scanning angle.

After the 30 to 2 degree running the samples were treated with ethylene glycol (CH_2OHCH_2OH), which forms an organic complex with the clays, and run through a 15 degree to two theta scanning angle. A noticeable expansion of montmorillonite can be measured, and there may be some expansion of halloysite and vermiculite.

The peak spacings were read from the chart graph paper in degrees two theta. These degrees were then converted to angstrom units giving d-spacing of the minerals. Conversions were made by the use of the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing", published by the U.S. Department of Commerce National Bureau of Standards Applied Mathematics Series-10. These values were then compared with values of the clay mineral d-spacing; also, the spacing of associated minerals of 2 micron and smaller size fraction.

It was found that the oriented slides gave the best pattern for clay mineral identification due to the basal orientation. The oriented samples gave the basal spacing clearly on the chart recorder while random oriented sample gave all the spacings. It was found that it is not necessary to remove the organic matter, carbonates, or iron when the goniometer chart recorder was used.

Stain Tests

Very little was done with stain testing except as a method of verification. The samples that showed an indication that there might be montmorillonite present were tested further with the benzidine staining method. Hendricks and

Alexander (1940) gave several methods for clay mineral identification by use of stain tests.

In the benezidine method of identification a small amount of benezidine was added to the sample and the color change was noted. When montmorillonite was present the sample changed to a blue color. Care should be taken in this method due to the fact organic matter forms a blue color also.

Differential Thermal Analysis

The furnace of the differential thermal apparatus was used as a method of heating slides for X-ray mineral identification. Differential thermal analysis was used also as a check of clay mineral identification and consisted of heating two samples (the unknown clay and Alundum, Al_2O_3) at a uniform temperature rate in a furnace. The reaction within the furnace was then recorded by means of two charts. One records the rate of temperature change and the other records the endothermic and exothermic reactions. By comparing the two charts the temperature of these reactions can be determined.

In the case of the samples that were run it was hard to make any definite mineral identification due to the mixed layering. The patterns were also affected by the carbonates and organic matter.

Preparation of Samples for Microscopic Study

The microscopic study was done on limestones, and since they are largely calcite it was necessary to remove the carbonates. The removal of the calcite was done by the use of hydrochloric acid, which left the material referred to as insoluble residue.

A sample of each limestone was run through the multiple hammer mill and then heated to remove any water that may have been present. One-hundred-fifty

grams of this size fraction was then taken for leaching with hydrochloric acid. The sample was then placed in a one-gallon wide mouth jar and treated with acid until effervesence ceased. Care was taken so that the sample did not effervese over the top of the jar due to the release of carbon dioxide. The sample was then washed several times with distilled water and decanted to remove as much of the acid as possible. After being washed in this manner, the samples were vacuum-filtered in a Buechner funnel and washed several more times to be sure of all acid removal.

After the acid treatment the samples were heated again and weighed to determine the amount of carbonates that were present in the original sample. This per cent was determined by taking the total weight of the sample minus the weight of the insoluble residue, which gives the weight of the carbonates. The weight of the carbonates was then divided by the total weight to determine the per cent of carbonates present.

After determination of the carbonate weight the samples were put back in distilled water and allowed to stand for 24 hours to allow rehydration. This sample was then mixed by the use of a magnetic mixer and Waring Blender for about five minutes each. After mixing the samples they were run through a U. S. # 270 screen (53 microns), which separated the sand fraction from the silt and clay. The sand fraction was washed several times to be sure that all the clay was removed.

The coarse material was then placed in a pyrex dish and transferred to an electric oven to dry. After drying it was run through a U. S. # 120 screen (125 microns) to remove the coarse residue. This coarse material was weighed and saved for mineral analysis. The sample that passed through the U. S. # 120 and did not pass through the U. S. # 270 was the material used in the heavy mineral separation.

Prior to the separation the minerals were heated to remove any moisture that may have been absorbed from the atmosphere. The minerals were then added to the bromoform and allowed to stand about two hours with periodic stirring to insure a complete separation.

Heavy mineral separation was done by the use of bromoform with a specific gravity of 2.7. The apparatus used consisted of three conical funnels, pinch-cocks, funnel stand, rubber tube, and Whatman #42 filter paper. The funnels were mounted one above the other with the upper funnel having a rubber tube and pinchcock to prevent the loss of bromoform. The lower funnel contained filter paper to catch the mineral grains. The heavy minerals were released first from the upper funnel and caught in the first lower funnel. This funnel was then moved and replaced by the second lower funnel in which the light minerals were caught on a filter paper.

After the separation the samples were washed with bromoform-ethyl alcohol and twice with ethyl alcohol. The bromoform-ethyl alcohol was saved and was used in several washings. The samples were then dried and weighed with per cent determination being made the same as for the carbonates.

Slides were then prepared from the heavy and light mineral fraction with the mounting medium being semi-liquid Canada Balsam with a refractive index of about 1.54. Slides were heated by use of a hot-plate and the Balsam was applied with a pyrex rod. The sample was then sprinkled on it and covered with a cover slide, with care being taken to prevent air bubbles. Special attention was given to the heavy mineral because of the small amount.

A petrographic study was then made by the use of a petrographic microscope and mechanical stage. The study included mineral identification and determination of mineral frequency by counting. A binocular study was also made of the coarse residue, particles greater than 125 microns.

NON-CARBONATE MINERALOGY OTHER THAN CLAYS

Light Minerals

The light mineral fraction was predominantly chalcedony with quartz, plagioclase, microcline and various forms of amorphous silica and ash in minor amounts. The chalcedony found was of three types: (1) fibrous chalcedony or chalcedony showing wavy extinction, (2) yellow-brown chalcedony, and (3) speckled or "salt and pepper" chalcedony.

More limonite staining was noticed in the samples that had been exposed to weathering than in samples such as the Neva, which was taken from a fresh road cut. In a great many cases the limonite staining was enough to make the mineral unrecognizable.

The speckled chalcedony showed blinking white and black specks as the stage of the microscope was rotated under crossed nicols. Wilbur (1956) stated that this type of chalcedony may be a transitional stage between the amorphous chalcedonic-opal and quartz. When the specks become large enough the chalcedony was called a quartz aggregate. Quartz was also found as individual grains. The types of formation seemed to affect the type of extinction of the quartz, wavy or snappy. In some cases quartz was found in the heavy mineral fraction as well as chalcedony, which in several cases made up a large part of the heavy fraction. This was attributed partly to limonite staining as well as to possible contamination by incorrect separation methods.

The feldspars and volcanic ash were found only in minor amounts, and in some cases they were absent.

Heavy Minerals

In most cases the heavy mineral fraction consisted of less than five-tenths of one per cent by weight. Most of the heavy fraction was of pyrite, celestite, and limonite. Limonite staining was abundant in all samples but the Neva, which was taken from a fresh exposure. In the samples that had undergone weathering, hematite was noticed to be forming at the expense of limonite.

Pyrite, FeS_2, found in this investigation was of several forms: (1) euhedral crystals, (2) a composite of small equidimensional crystals, and (3) as coating on other grains. The pyrite seemed to be the major source for the limonite. All stages of limonite alteration were found.

Other heavy minerals found were chlorite, hornblend, muscovite, zircon, biotite, and rutile. Generally all of these minerals formed only a small part of the heavy mineral fraction.

Coarse Residue

The coarse residue was composed in a large part of chalcedony, which was of the replacement type or fragmental type. Pyrite and limonite was also noticed with all intermediate stages of alteration.

Detrital quartz exhibiting subrounded grains and a good degree of sorting was observed in that all grain were nearly the same size. The rounding indicates the amount of weathering and reworking that the quartz has undergone.

X-RAY DETERMINATION OF CLAY MINERALS

Blue Rapids Shale

The X-ray analysis of the Blue Rapids showed illite to be the major clay with chlorite, montmorillonite-illite, montmorillonite-chlorite-illite, and

Table 3. Summary of light mineral analysis of insoluble residue in the size range from 53-125 microns and carbonate per cent.

Sample Number	Formation or Member	Per cent of Total weight	Per cent of Carbonates	Per cent of Quartz	Per cent of Plagioclase	Per cent of Orthoclase	Per cent of Microcline	Per cent of Volcanic Ash	Limonite Staining	Undefiable	Per cent of Chalcedony	Limonite Stained Chalcedony
3-4	Eskridge Sh. (Ls. Lense)	19.27	80.6	2	3				5		33	57
4-1	Neva Ls.	7.1	92.9		4	2					52	42
4-2	Neva Ls.	26.0	73.9	5	3						63	29
4-3	Neva Ls.	3.7	96.3	6				4			85	5
4-5	Neva Ls.	16.4	83.6	7	5	1		3	1		79	14
4-7	Neva Ls.	15.9	84.0	9	6						76	9
5-2	Johnson Sh. (Ls. Lense)	28.7?	71.3?	12	1			1			81	5
5-6	Johnson Sh. (Ls. Lense)	12.4	87.2	7		1	2				76	9
6-1	Glenrock Ls.	16.9	83.0	1	1						78	20
8-1	Howe Ls.	14.9	85.0	20	11	8					39	18
9-3	Roca Sh. (Ls. Lense)	12.1	87.9	8	1			3			8	80
9-5	Roca Sh. (Ls. Lense)	10.1	89.9	2	4	3					23	68
10-1	Burr Ls.	6.6	93.4	6	4	2					40	48
10-3	Burr Ls.	6.2	93.8	22	2						53	24

Table 4. Summary of heavy mineral analysis of insoluble residue in the size range from 53-125 microns. Heavy mineral fraction was less than five-tenths of one per cent of the total weight.

Sample Number	Formation or Member	Magnetite	Pyrite	Limonite Coated Pyrite	Unrecognizable Limonite Coated	Muscovite	Celestite	Tourmaline	Rutile	Hornblende	Zircon	Chlorite	Hematite Coated Grains	Garnet	Remarks (Light mineral contamination)
3-4	Eskridge Sh. (Ls. Lense)		6	44	10	14	13						13		Chalcedony and Quartz
4-1	Neva Ls.	3	30	28		11	10		1	2			15		Chalcedony
4-2	Neva Ls.		2	26	16	2	54			2		4			Chalcedony
4-3	Neva Ls.	2	4	15		37	40					2			Chalcedony
4-5	Neva Ls.	5	14	57		1	8						15		Chalcedony
4-7	Neva Ls.		10	25		4	31				4	3	23		Chalcedony
5-2	Johnson Sh. (Ls. Lense)		18	28			8			2	1		43		Chalcedony
5-6	Johnson Sh. (Ls. Lense)		4	8		9	78			1			1		Chalcedony
6-1	Glenrock Ls.		9	28	7		38						18		Chalcedony and Quartz
8-1	Howe Ls.		5	18		10	61					3	3		Chalcedony and Quartz
9-3	Roca Sh. (Ls. Lense)	2	23	40		10	16				2	1	1		Chalcedony
9-5	Roca Sh. (Ls. Lense)	3	15	23	10	3	14						32		Chalcedony
10-1	Burr Ls.		2	16	9	43	20					4	6		Chalcedony
10-3	Burr Ls.		16	53		16	6	2		5	1			1	Chalcedony

Table 5. Summary of coarse residue analysis of insoluble residue greater than 125 microns in size.

Sample Number	Formation or Member	Per cent of Total Weight	Chalcedonic Fragments	Chalcedonic Fossil Frag.	Detrital Quartz	Pyrite	Limonite Coated	Organic Residue	Muscovite Flakes	Gray Shale	Magnetite
3-4	Eskridge Sh. (Ls. Lense)	.13	Major		XX	Trace	X	Trace	Trace		
4-1	Neva Ls.	.013	Major		X	XX	XX	XX	Trace		Trace
4-2	Neva Ls.	.13	Major	XX	Trace		Trace	XX			
4-3	Neva Ls.	.01	Major	X	XX	Trace	X	XX	XXX		Trace
4-5	Neva Ls.	.02	XXX		Major	X	XX	Trace	X		X
4-7	Neva Ls.	.1	Major		XX	X	XX	Trace	X		
5-2	Johnson Sh. (Ls. Lense)	.03	Major		X	X	X		Trace		
5-6	Johnson Sh. (Ls. Lense)	.43	XX		Major		Trace	Trace	X		
6-1	Glenrock Ls.	.1	Major	X	XX	X	Trace	Trace	X		
8-1	Howe Ls.	.1	Major		X	X	X	Trace	X		
9-3	Roca Sh. (Ls. Lense)	.01	Major		X	X	XX	Trace			Trace
9-5	Roca Sh. (Ls. Lense)	.013	Major	X	X	X	XX	XX	Trace		Trace
10-1	Burr Ls.	.03	Major	X	Trace		XX		Trace		
10-3	Burr Ls.	.01	Major	X	XX	XX	XX	Trace	X	X	Trace

Scale of Abundance: Major, XXX, XX, X, Trace.

montmorillonite-chlorite being present in all the samples tested. Only minor amounts of quartz and calcite were found. There did not seem to be any increase in the montmorillonite content toward the chert bearing Crouse limestone below the Blue Rapids.

Eskridge Shale

Samples of the Eskridge shale showed illite to be the major clay mineral; and the minor clay minerals to be chlorite, montmorillonite-illite, montmorillonite-chlorite, chlorite-montmorillonite, and montmorillonite-chlorite-illite. No quartz was found in the -2 micron non-clay mineral fraction; but calcite was very abundant in 3-2 and 3-7, which were limestone lenses. A super-lattice clay was found in sample 3-5, and free montmorillonite in sample 3-8. The petrographic study of the limestone lense, 3-7, showed a high pyrite and hematite stained grain content. It was assumed the pyrite supplied the iron through weathering to form the iron-rich chlorites, which were found in all the samples.

McPherron (1956) stated that under a marine environment there was a reciprocal relationship between the quartz and chlorite in the shales he examined, with the quartz being used in the formation of chlorite. In the limestones that were run in this investigation this reciprocal relationship was not found to be the case. Chlorite and quartz were found in all cases except in the Glenrock. It was assumed, therefore, that the iron-rich chlorites found in the limestones in this investigation were not associated with the quartz. The iron for these iron-rich chlorites was probably derived from the weathering of the pyrite.

Neva Limestone

A petrographic and X-ray diffraction analysis were run on the Neva, with the samples being both weathered and fresh. It was possible by relating the weathered to the unweathered in these samples to further substantiate the chlorite-pyrite-quartz relationship. The major clay mineral was illite in all cases but 4-4, which showed the montmorillonite-chlorite-illite to be the major clay mineral. The montmorillonite found in samples 4-1, 4-2, and 4-6 may have been related to the ash and chert. Ash and chert were both found in 4-3, 4-4, and 4-5 of the Neva. There was a lack of chlorite in many cases in the fresh samples as well as a lack of chlorite-montmorillonite. Fresh samples of the Neva also showed very little montmorillonite-illite, which indicated the assymetry of the illite peak was due to the weathering of the illite to montmorillonite as stated by Harrison and Murray at the 1957 Clay Mineral Conference.

Salem Point Shale

The major clay mineral was illite; and the minor clay minerals were chlorite, montmorillonite-illite, and a super-lattice clay. The -2 micron non-clay fraction showed calcite and quartz in minor amounts, which also indicates that the quartz was not used in the chlorite formation.

Burr Limestone

The Burr differed from the Salem Point in the clay mineralogy in that it had no super-lattice clay minerals present. Both calcite and quartz were present, with the calcite being in large amounts in 10-1 and 10-3. The petrographic studies showed the weathering sequence, pyrite-limonite-hematite; also, a large percent of celestite and limonite stained chalcedony was found.

Roca Shale

The Roca was a varigated shale, with illite being the major clay mineral. Chlorite, chlorite-montmorillonite, montmorillonite-chlorite-illite, montmorillonite-illite was found in all samples; and a super-lattice clay was found in 9-1 and 9-2. There seemed also to be some relation between the super-lattice clay and the weathering stage, with the super-lattice clay being found only in the samples showing some weathering. A petrographic study was run on 9-3 and 9-5, which showed the pyrite to hematite weathering sequence further substantiating the chlorite and chlorite-quartz formation ideas.

Howe Limestone

The clay minerals present were the same as those of the Neva and Burr with the exception of the super-lattice clay, which may have been masked by the calcite in the Neva and Burr. The Howe also showed a large quartz and chlorite content, which tends to indicate that the quartz was not associated with the chlorite formation in this case. A high celestite and hematite coated grain content was noticed in the petrographic study, which indicates a high amount of weathering.

Glenrock Limestone

The Glenrock showed a lack of both chlorite and quartz. The major clay mineral was illite, with montmorillonite-illite and montmorillonite-chlorite-illite being present in minor amounts. The petrographic study indicated a high pyrite, hematite, and celestite content, which should have indicated a high chlorite content. It may have been possible though that the chlorite peak was masked due to the exceptionally high calcite content.

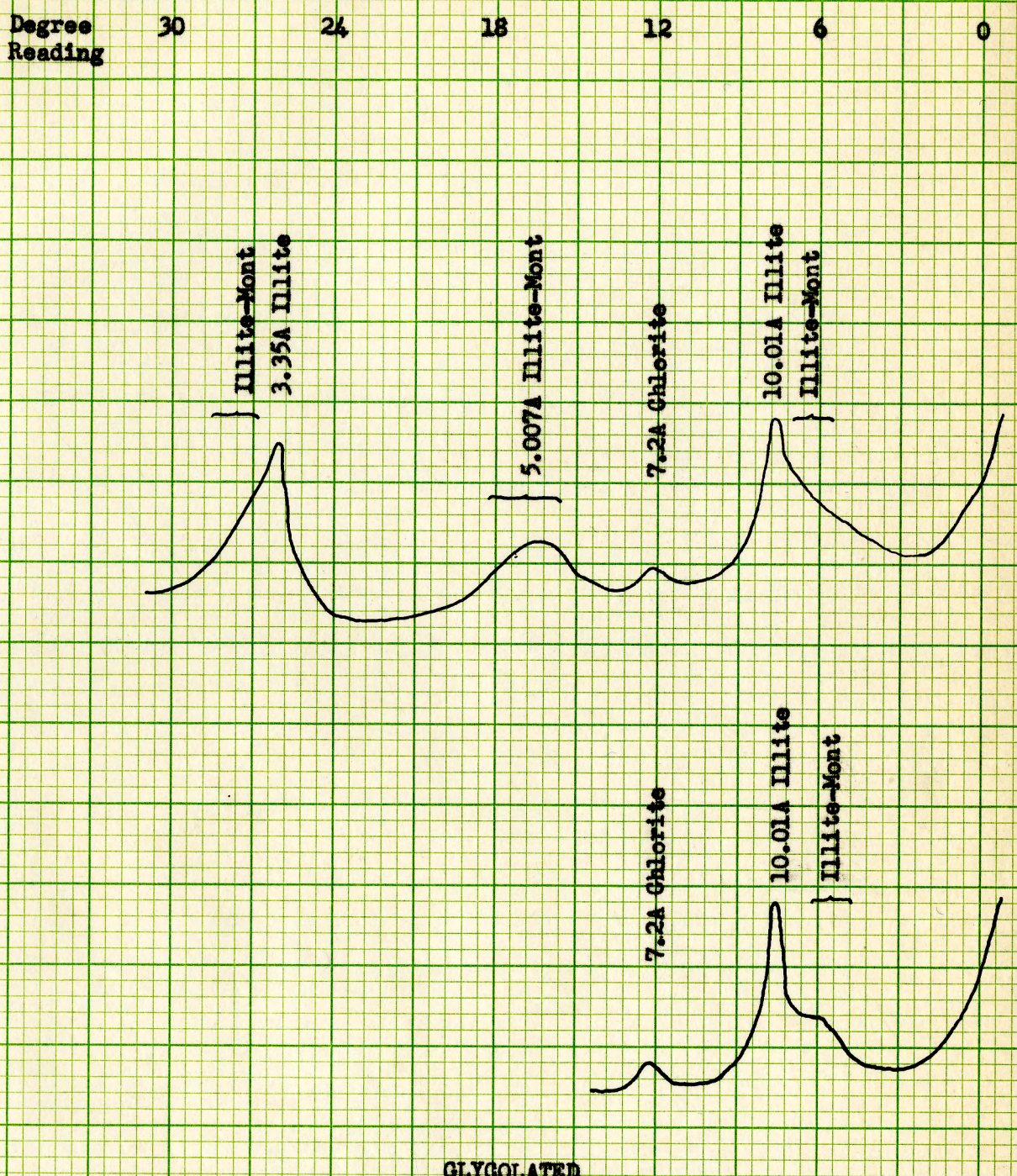
Johnson Shale

The clay mineral relationship was the same as the Roca with the superlattice clays being present in all samples except 5-2 and 5-6, which were limestone lenses. The clay minerals present were illite, montmorillonite-illite, chlorite, montmorillonite-chlorite, chlorite-montmorillonite, and montmorillonite-chlorite-illite. The petrographic study of the limestone ledges, 5-2 and 5-6, indicated an exceptionally high celestite content with the other minerals being present in about the same ratio.

EXPLANATION OF PLATE III

X-ray spectometer tracing of general X-ray curves showing the conversion of illite to illite-montmorillonite random interlayered clay. The illite-montmorillonite shows assymetry on the low-angle side of the 001 peak of illite, assymetry on the high-angle side of the 003 peak, and broading of the 002 peak. Upon glycolation there is a slight movement of the illite-montmorillonite on the 001 peak.

PLATE III

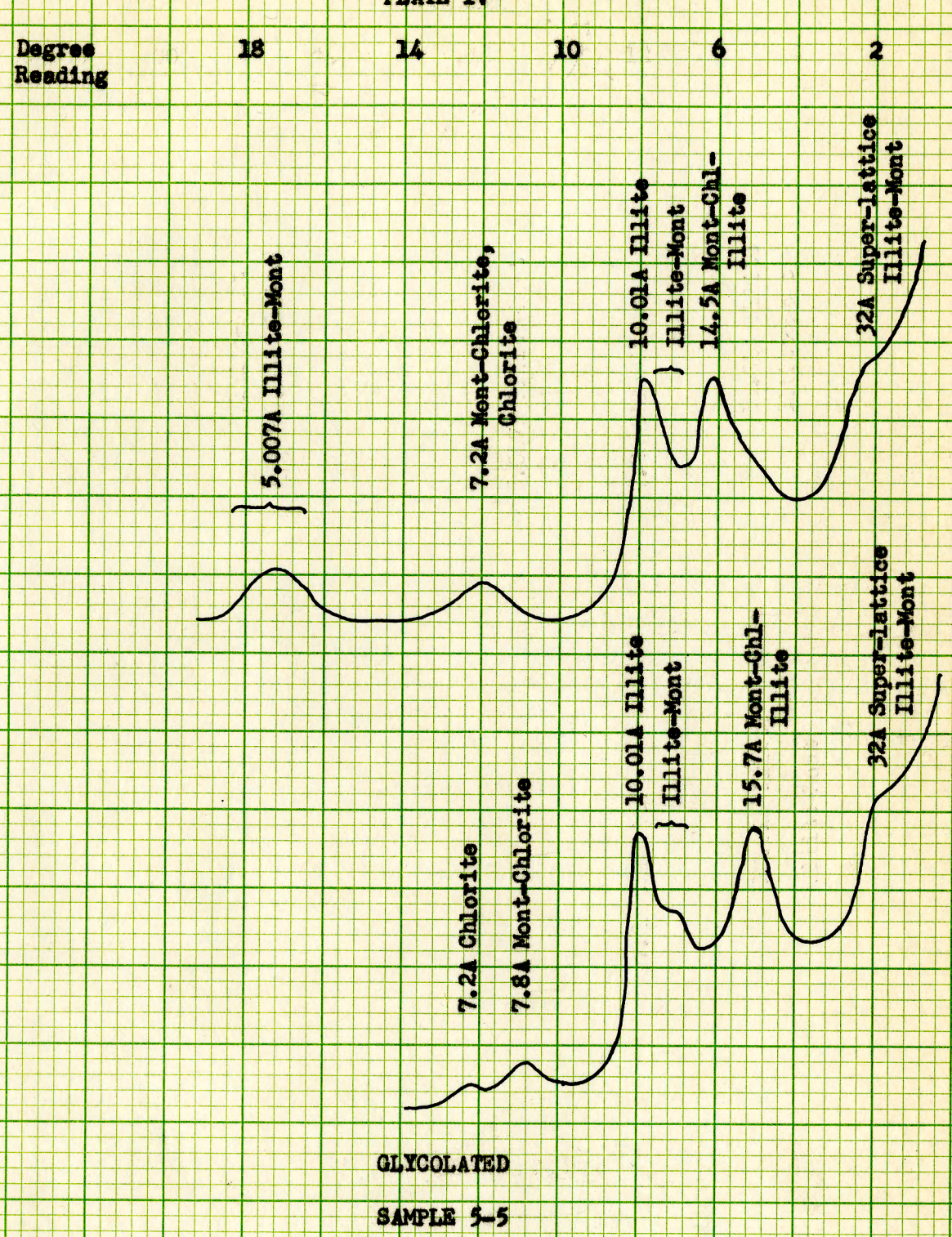


GLYCOLATED

EXPLANATION OF PLATE IV

X-ray spectometer tracing of 5-5, Johnson Shale, showing the expansion of the montmorillonite-chlorite, chlorite-montmorillonite, illite-montmorillonite, and montmorillonite-chlorite-illite. A further explanation shown in Plates V and VI.

PLATE IV



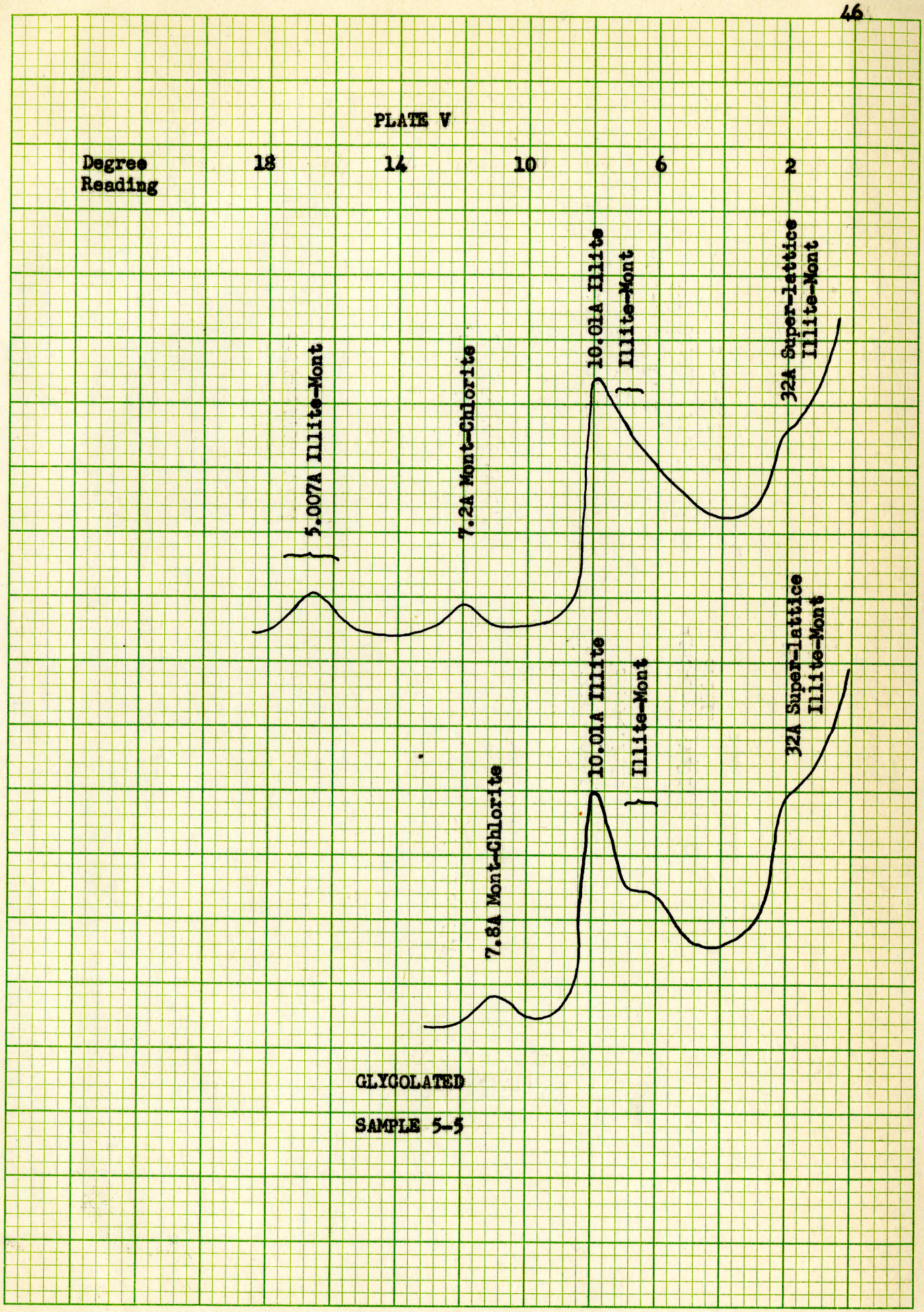
GLYCOLATED

SAMPLE 5-5

EXPLANATION OF PLATE V

X-ray spectrometer tracing of 5-5, Johnson Shale, showing expansion after treatment and heating with HCl, and that the 7.2A peak after glycolation is completely destroyed indicating the presence of chlorite.

PLATE V



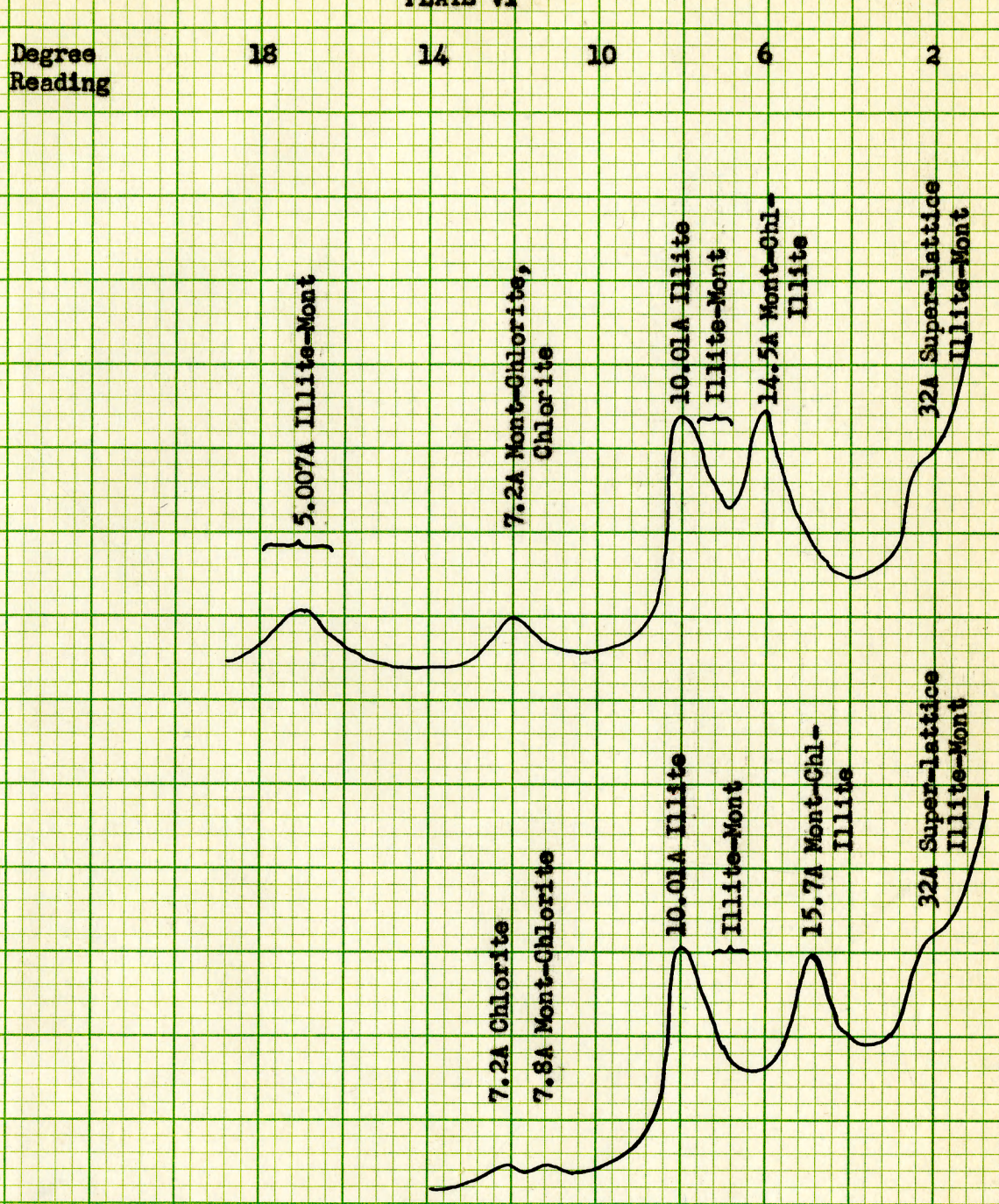
GLYCOLATED

SAMPLE 5-5

EXPLANATION OF PLATE VI

X-ray spectrometer tracing of 5-5, Johnson Shale, showed no movement of the 7.2A peak when treated and heated with NH_4Cl. If vermiculite was present it should have shifted down the 7.2A peak as well as some movement of the 6.2A peak toward the larger angstrom readings should have been noticed.

PLATE VI



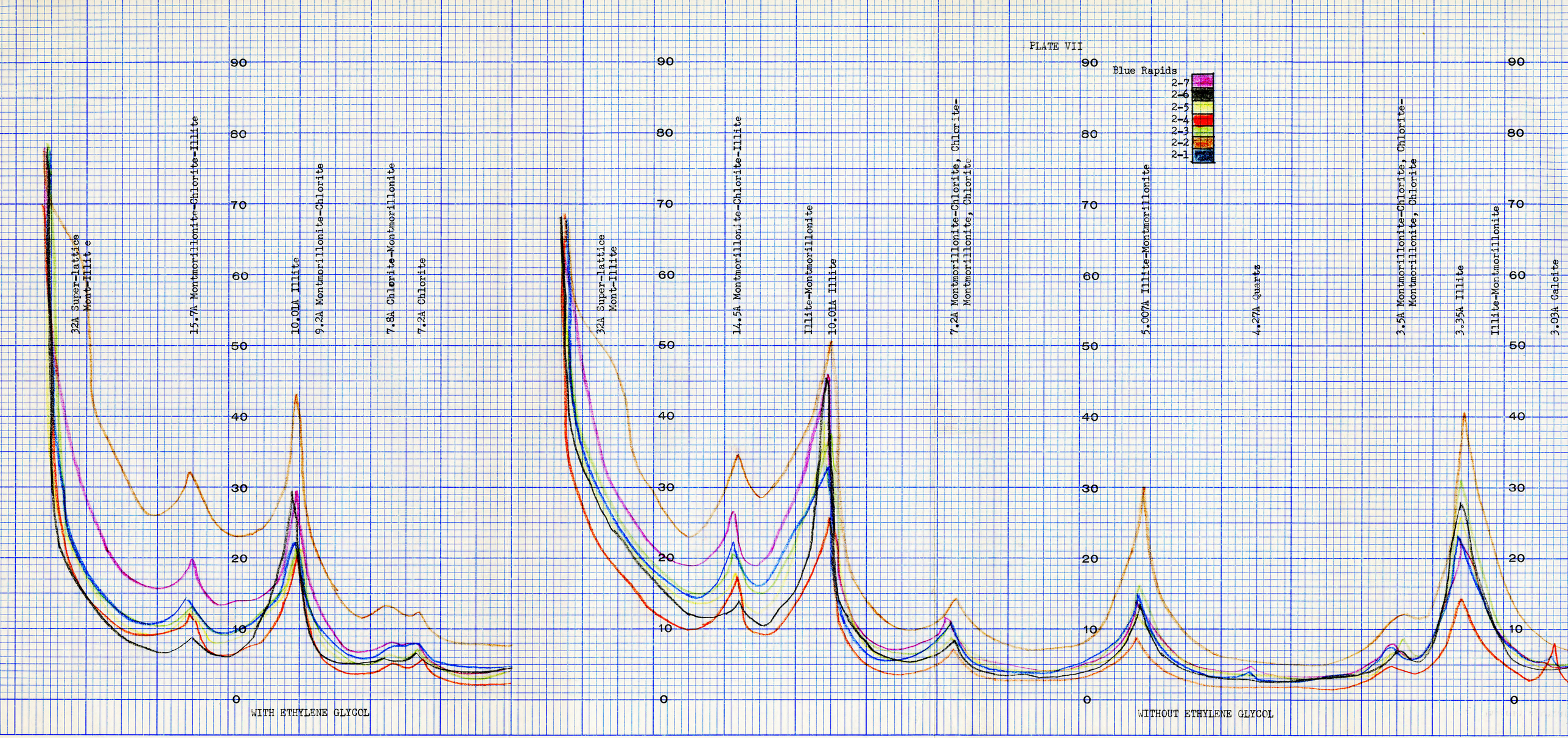
GLYCOLATED

SAMPLE 5-5

EXPLANATION OF PLATE VII

X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Blue Rapids Shale.

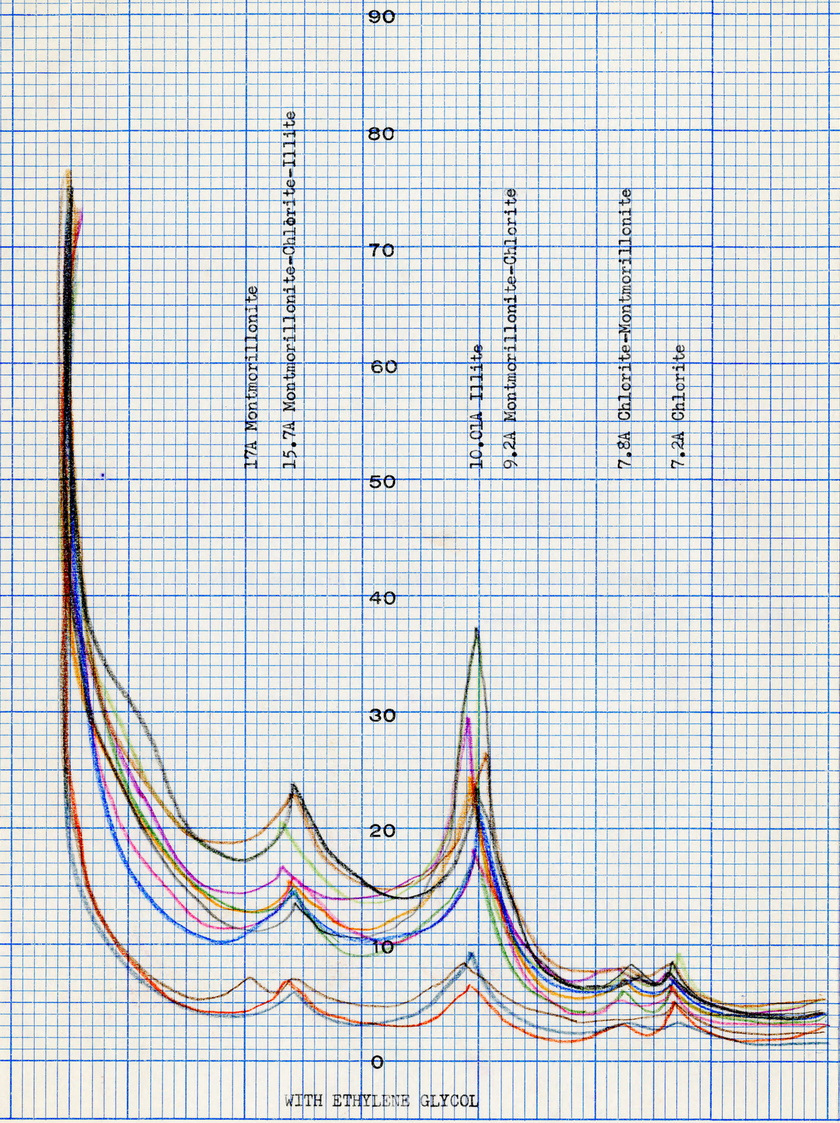
PLATE VII


Blue Rapids
2-7
2-6
2-5
2-4
2-3
2-2
2-1
32A Super-lattice Mont-Illite
15.7A Montmorillonite-Chlorite-Illite
10.01A Illite
9.2A Montmorillonite-Chlorite
7.8A Chlorite-Montmorillonite
7.2A Chlorite
WITH ETHYLENE GLYCOL
32A Super-lattice Mont-Illite
14.5A Montmorillonite-Chlorite-Illite
Illite-Montmorillonite
10.01A Illite
7.2A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
5.007A Illite-Montmorillonite
4.27A Quartz
3.5A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
3.35A Illite
Illite-Montmorillonite
3.03A Calcite
WITHOUT ETHYLENE GLYCOL
0
10
20
30
40
50
60
70
80
90

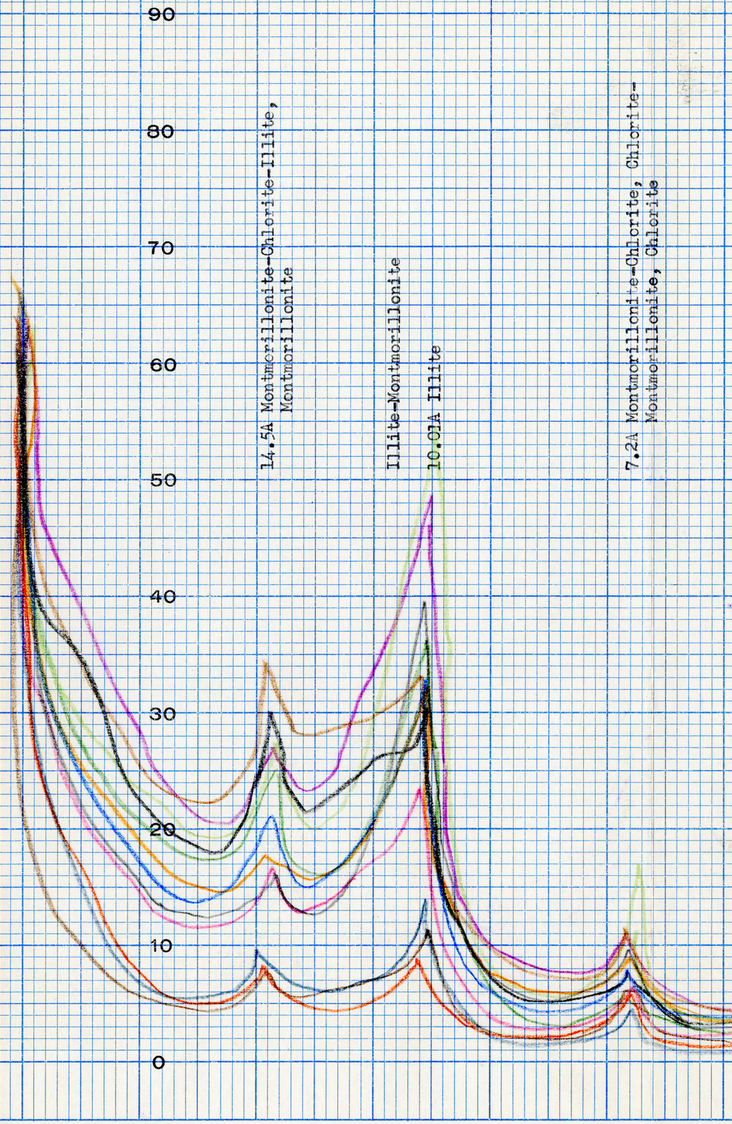
EXPLANATION OF PLATE VIII

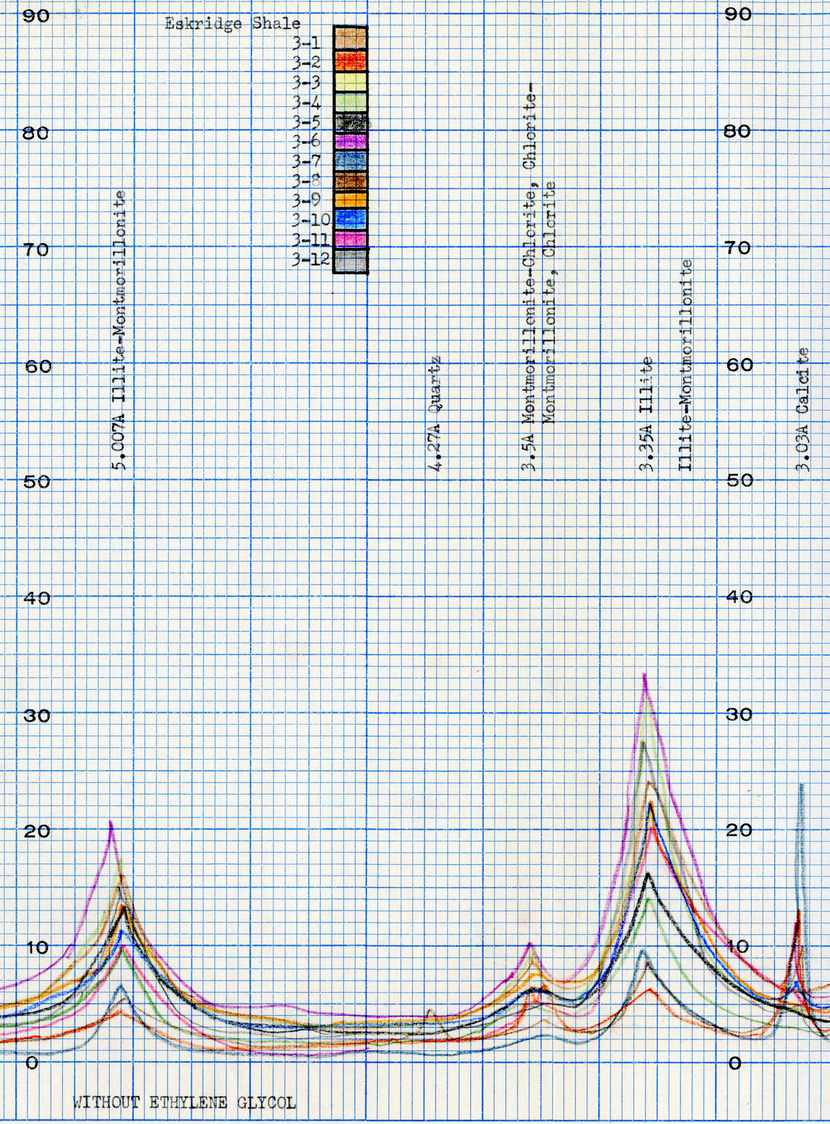
X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Eskridge Shale.

PLATE VIII



WITH ETHYLENE GLYCOL

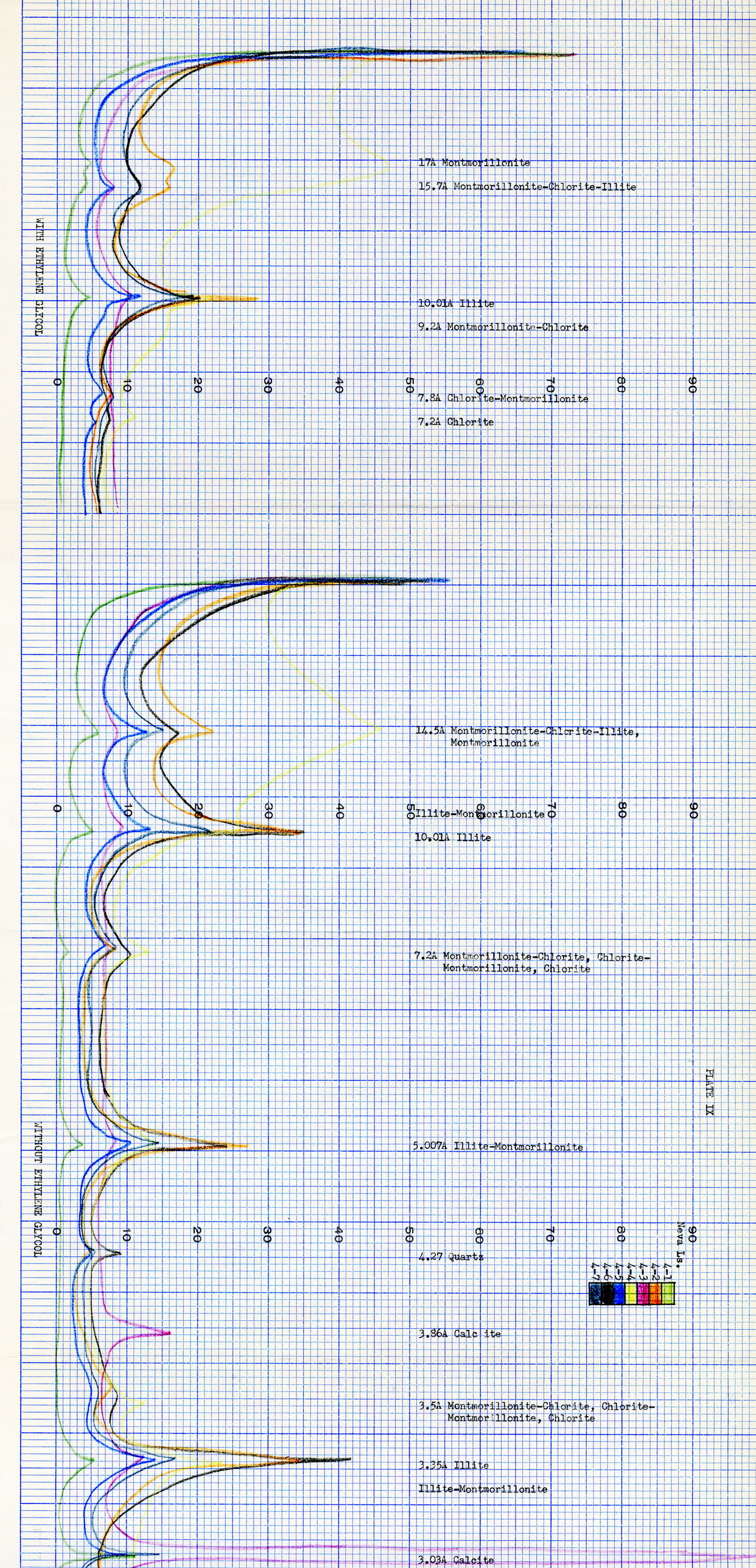




WITHOUT ETHYLENE GLYCOL

EXPLANATION OF PLATE IX

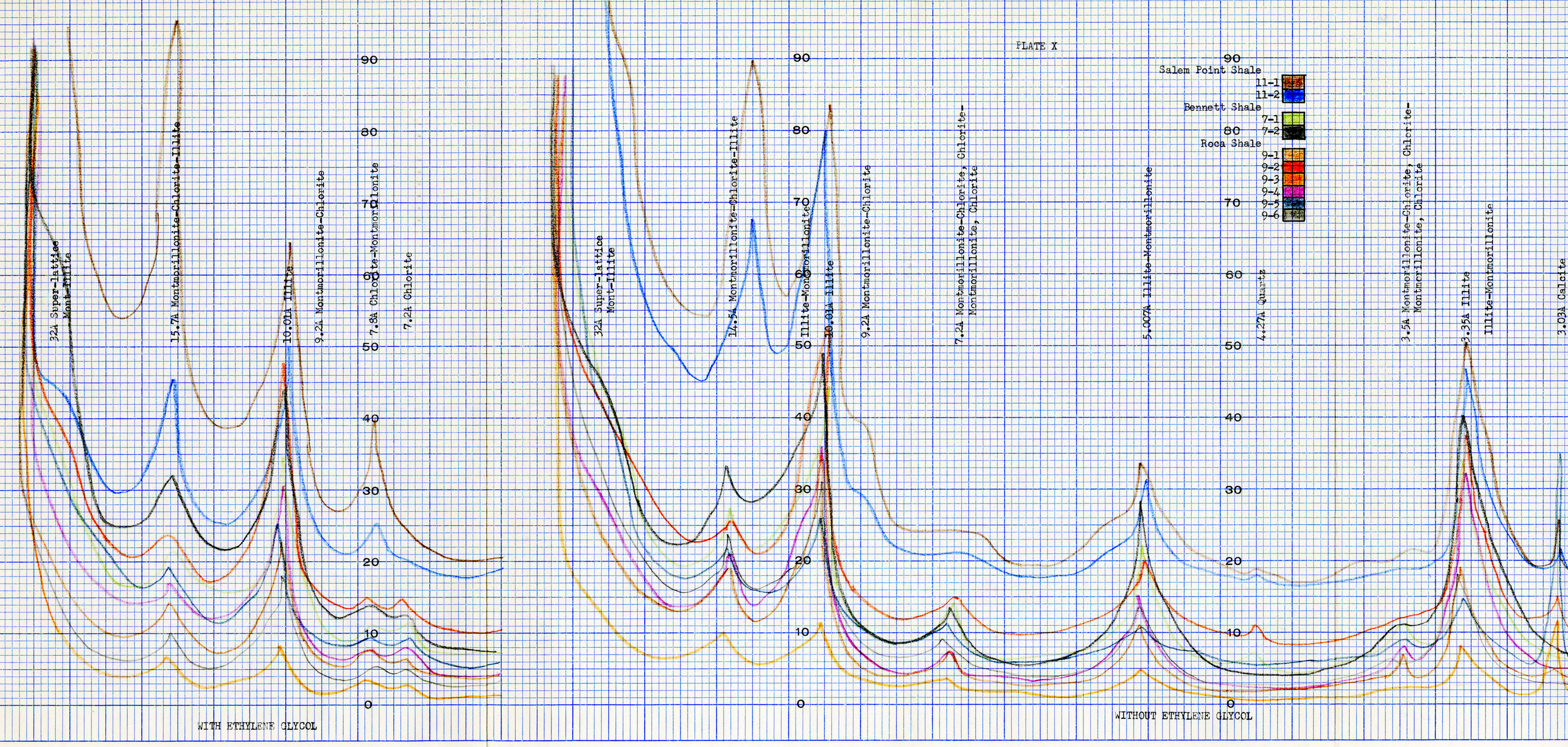
X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Neva Limestone.


WITH ETHYLENE GLYCOL
17A Montmorillonite
15.7A Montmorillonite-Chlorite-Illite
10.01A Illite
9.2A Montmorillonite-Chlorite
7.8A Chlorite-Montmorillonite
7.2A Chlorite
0
10
20
30
40
50
60
70
80
90
14.5A Montmorillonite-Chlorite-Illite, Montmorillonite
Illite-Montmorillonite
10.01A Illite
7.2A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
WITHOUT ETHYLENE GLYCOL
5.007A Illite-Montmorillonite
4.27 Quartz
3.86A Calcite
3.5A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
3.35A Illite
Illite-Montmorillonite
3.03A Calcite
Neva Less
PLATE IX

EXPLANATION OF PLATE X

X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Salem Point Shale, Bennett Shale, and Roca Shale.

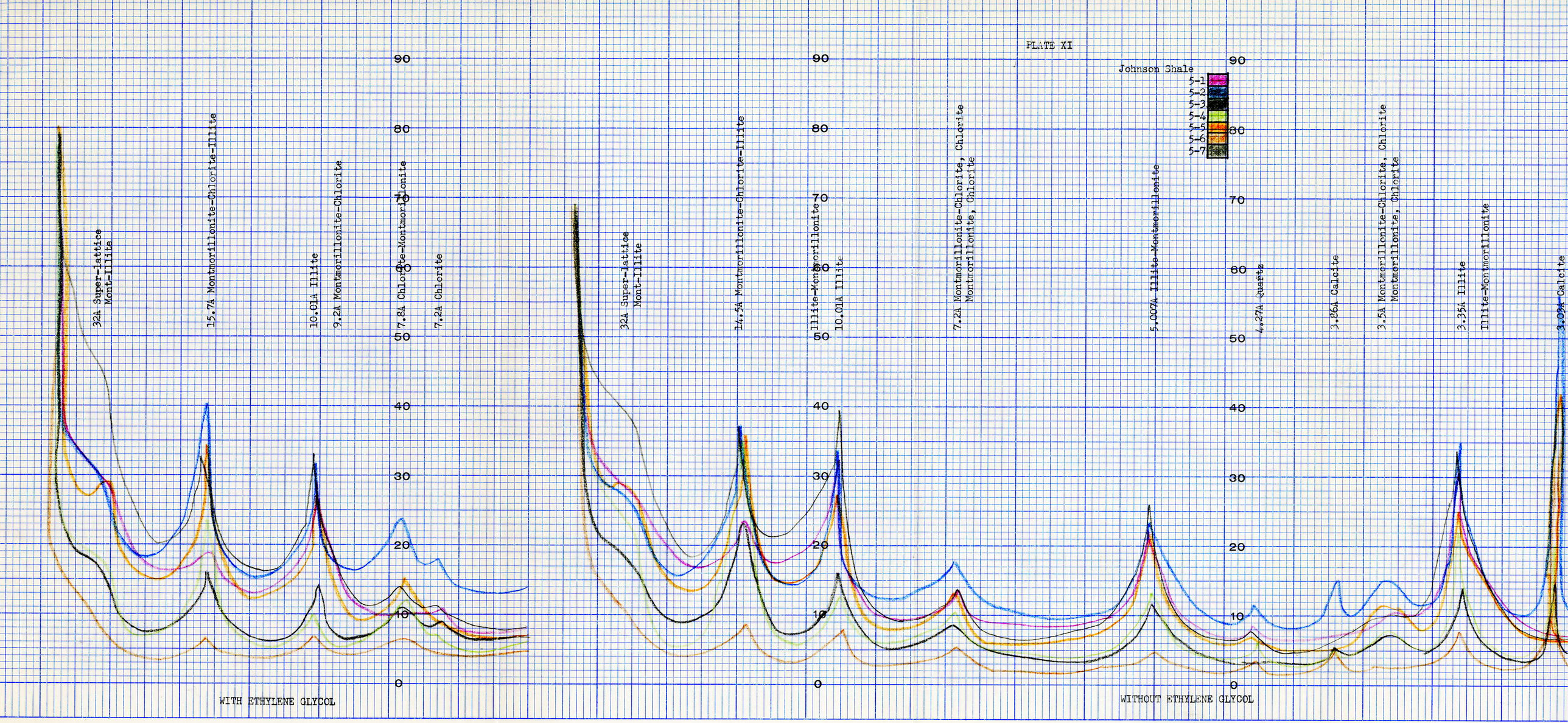
PLATE X


32A Super-lattice Mont-Illite
15.7A Montmorillonite-Chlorite-Illite
10.01A Illite
9.2A Montmorillonite-Chlorite
7.3A Chlorite-Montmorillonite
7.2A Chlorite
WITH ETHYLENE GLYCOL
32A Super-lattice Mont-Illite
14.5A Montmorillonite-Chlorite-Illite
Illite-Montmorillonite
10.01A Illite
9.2A Montmorillonite-Chlorite
7.2A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
5.007A Illite-Montmorillonite
4.27A Quartz
3.54A Montmorillonite-Chlorite, Chlorite-Montmorillonite, Chlorite
3.35A Illite
Illite-Montmorillonite
3.03A Calcite
WITHOUT ETHYLENE GLYCOL
Salem Point Shale
11-1
11-2
Bennett Shale
7-1
7-2
Roca Shale
9-1
9-2
9-3
9-4
9-5
9-6
0
10
20
30
40
50
60
70
80
90

EXPLANATION OF PLATE XI

X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Johnson Shale.

PLATE XI


Johnson Shale
5-1
5-2
5-3
5-4
5-5
5-6
5-7
32A Super-lattice Mont-Illite
15.7A Montmorillonite-Chlorite-Illite
10.01A Illite
9.2A Montmorillonite-Chlorite
7.8A Chlorite-Montmorillonite
7.2A Chlorite
32A Super-lattice Mont-Illite
14.5A Montmorillonite-Chlorite-Illite
Illite-Montmorillonite
10.01A Illite
7.2A Montmorillonite-Chlorite, Chlorite Montmorillonite, Chlorite
5.007A Illite-Montmorillonite
4.27A Quartz
3.86A Calcite
3.5A Montmorillonite-Chlorite, Chlorite Montmorillonite, Chlorite
3.35A Illite
Illite-Montmorillonite
3.03A Calcite
0
10
20
30
40
50
60
70
80
90
WITH ETHYLENE GLYCOL
WITHOUT ETHYLENE GLYCOL

EXPLANATION OF PLATE XII

X-ray diffractometer smooth line tracings of oriented slides of the clay fraction of the Burr Limestone, Howe Limestone, and Glenrock Limestone.

PLATE XII

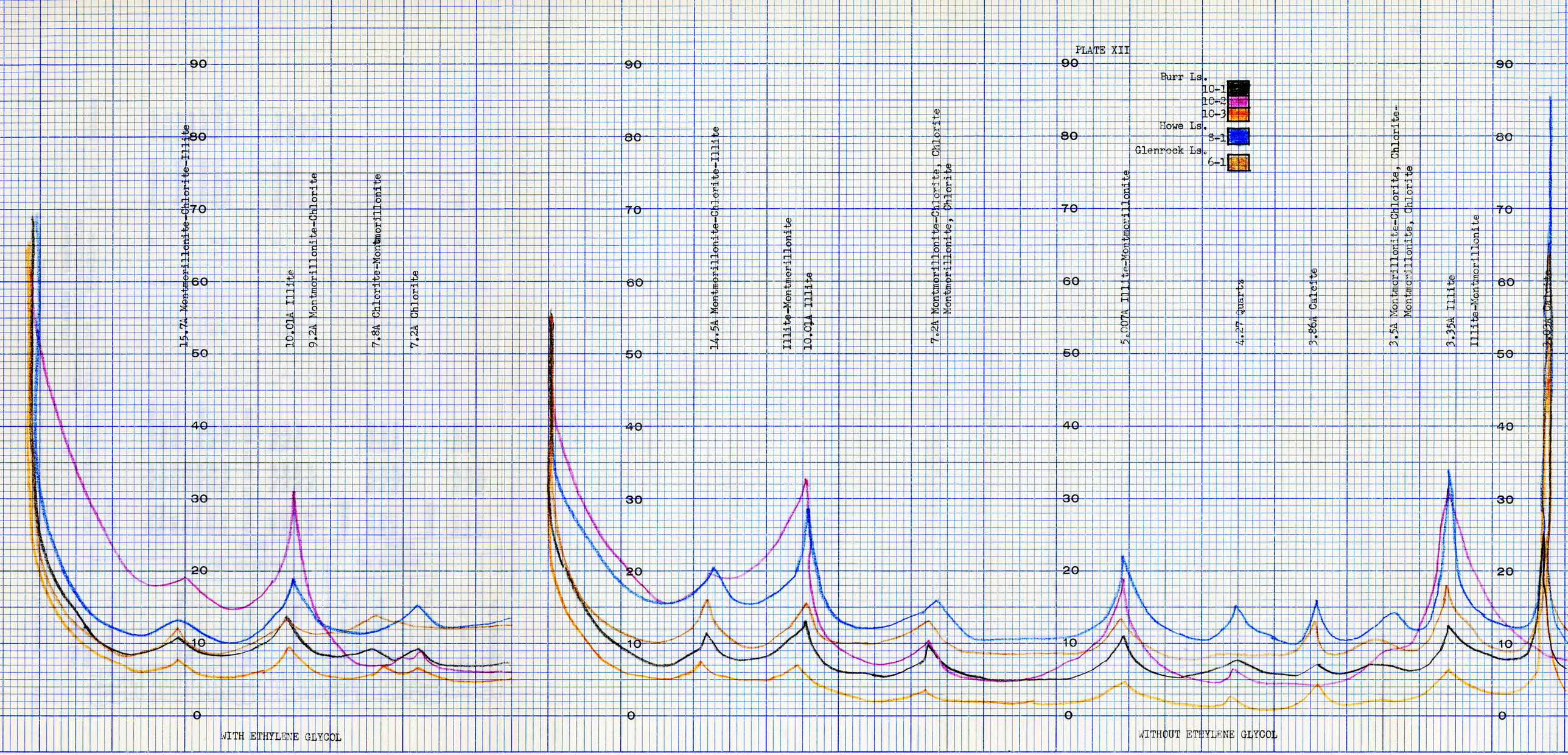
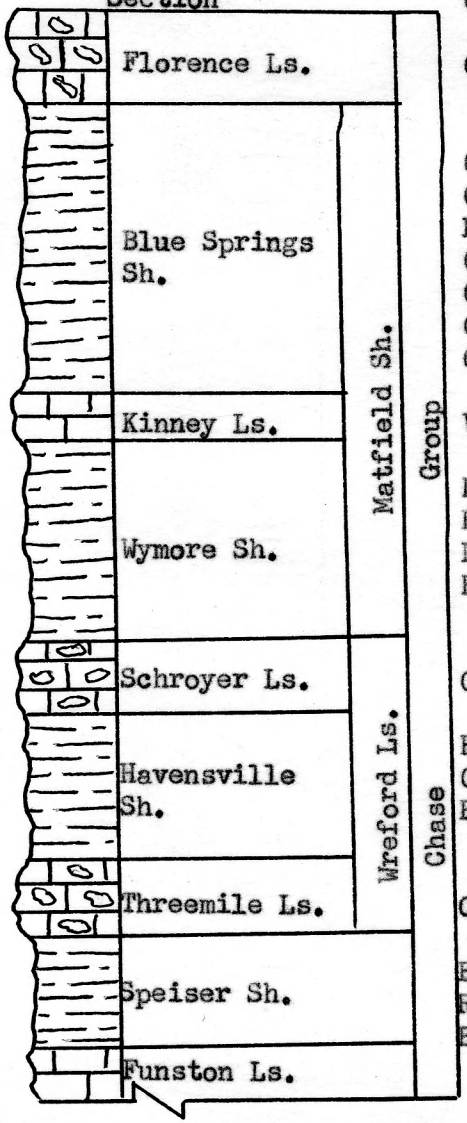
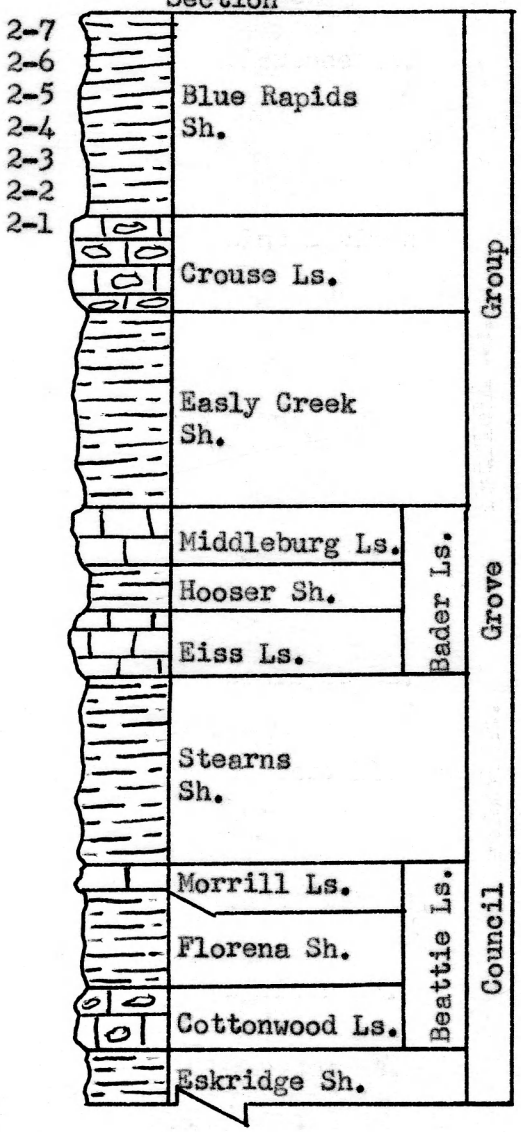

Burr Ls.
10-1
10-2
10-3
Howe Ls.
8-1
Glenrock Ls.
6-1
15.7A Montmorillonite-Chlorite-Illite
10.0A Illite
9.2A Montmorillonite-Chlorite
7.8A Chlorite-Montmorillonite
7.2A Chlorite
14.5A Montmorillonite-Chlorite-Illite
Illite-Montmorillonite
10.0A Illite
7.2A Montmorillonite-Chlorite, Chlorite
Montmorillonite, Chlorite
5.00A Illite-Montmorillonite
4.27 Quartz
3.86A Calcite
3.5A Montmorillonite-Chlorite, Chlorite-
Montmorillonite, Chlorite
3.35A Illite
Illite-Montmorillonite
3.03A Calcite
90
80
70
60
50
40
30
20
10
0
WITH ETHYLENE GLYCOL
WITHOUT ETHYLENE GLYCOL

Table 6. Summary of the clay minerals present in the shales and limestones.



Color	Illite	Chlorite	Illite	Chlorite C/V	Chlorite V/C	Montmorillonite Illite	Quartz	Calcite
CHERTY								
Gray	Major	Abundant	P	P	P	P	Abundant	Minor
Green	Major	Minor			P			Major
Red	Major	Abundant	P		P		Abundant	Major
Green	Major				P			Minor
Green	Major	Abundant	P	P			Abundant	Minor
Gray	Major	Major	P	P		P	Abundant	Abundant
Gray	Major	Major		P		P	Trace	Minor
VOLCANIC GLASS SHARDS								
Buff	Major	Major		P		P	Abundant	Minor
Buff	Major	Major	P	P			Abundant	Major
Buff	Major	Minor		P			Trace	Major
Buff	Major				P	P	Minor	Major
CHERTY								
Buff	Major	Minor			P	P	Minor	
Gray	Major	Minor			P	P	Trace	
Buff	Major	Trace			P	P	Minor	
CHERTY								
Buff	Major	Trace	P		P	P	Minor	
Red	Major	Minor			P			Abundant
Buff	Major				P			

Table 6. (cont.)

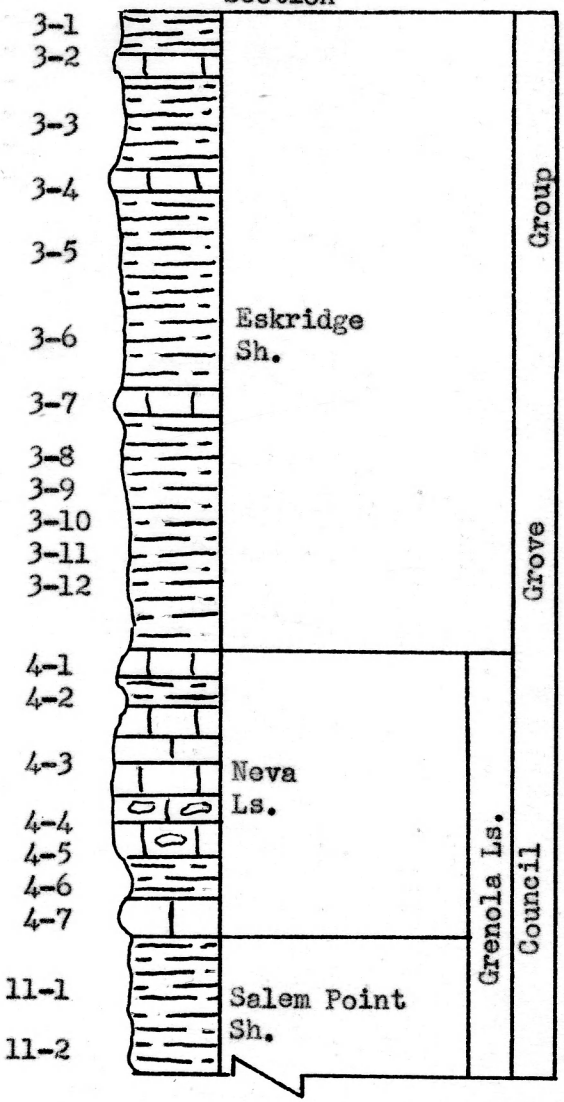


Color	Illite	Chlorite	Chlorite:Illite	Chlorite: Vermiculite C/V	Montmorillonite: Vermiculite V/C	Montmor-illonite: Illite	Quartz	Calcite	Mont.Chl. Ill. *	Mont.Chl. *
Gray	Major	P				P	Minor	Minor	P	P
Red	Major	P				P			P	P
Gray	Major	P				P			P	P
Gray	Major	P				P	Major		P	P
Green	Major	P				P			P	P
Red	Major	P				P			P	P
Green	Major	P				P	Minor	Minor	P	P
LOCALLY CHERTY										
Buff	Major		P		P	P	Abundant	Trace		
Buff	Major	Minor	P	P		P	Trace	Trace		
Green	Major	Minor	P	P				Abundant		
Red	Major	Minor	P	P	P			Major		
Buff	Major	Minor	P	P	P		Trace			
Gray	Major	Abundant	P	P	P		Minor	Major		
Red	Major	Abundant		P	P		Minor	Minor		
Green	Major	Minor	P	P	P			Minor		
Gray	Major	Abundant	P	P			Minor	Major		
Gray	Major	Abundant	P	P	P			Major		
Gray	Major	Abundant	P		P		Trace	Major		
Buff	Major			P	P					
Gray	Major		P	P			Trace	Trace		
Buff	Major	Abundant	P	P		P	Minor	Abundant		
Gray	Major	Abundant	P	P		P		Minor		
CHERTY										

SCALE 1"=20', Florence Ls. through the Cottonwood Ls.

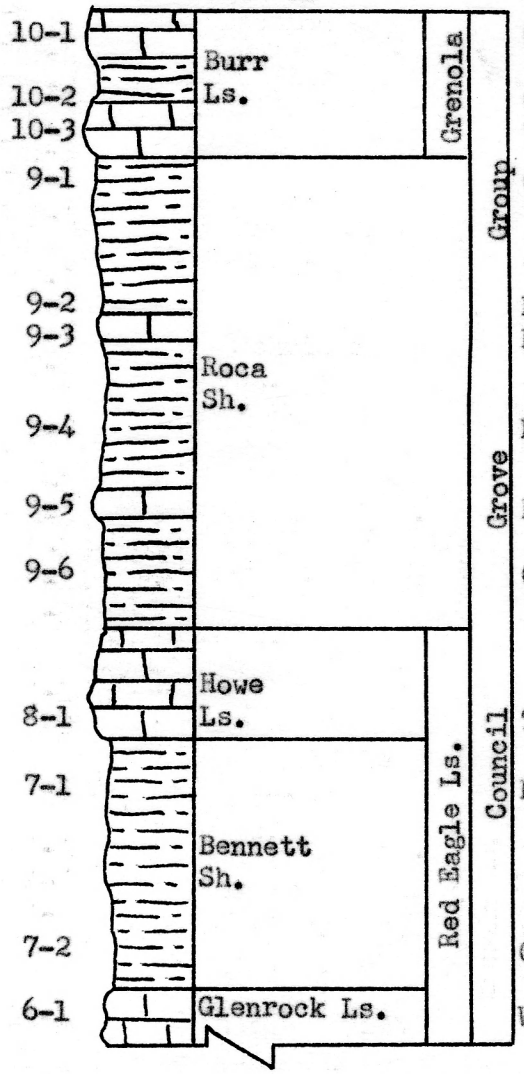
* Indicates work done during this investigation.

Table 6. (cont.)



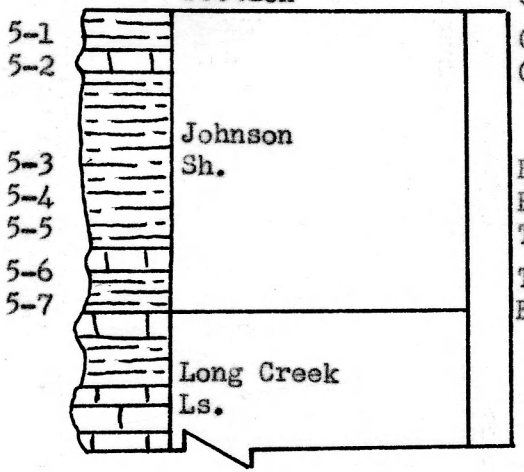
	Color	Illite	Chlorite	Montmor-Chlorite M/C	Montmor-Chlorite C/M	Montmor-Illite	Montmor-Illite	Super-lattice Mont-Ill	Montmor-illonite	Calcite	Quartz
3-1	Brown	Major	P		P	P	P				
3-2	Purple	Major	P		P	P	P			Major	
3-3	Gray	Major	P		P	P	P			Minor	
3-4	Gray	Major	P	P	P	P	P				
3-5	Green	Major	P	P	P	P	P	P		Minor	
3-6	Brown	Major	P	P	P	P	P				
3-7	Gray	Major	P	P	P	P	P			Major	
3-8	Tan	Major	P	P		P			P	Major	
3-9	Purple	Major	P	P	P	P	P			Minor	
3-10	Gray	Major	P	P	P	P	P			Minor	
3-11	Gray	Major	P		P	P	P			Minor	
3-12	Red	Major	P		P	P	P				
4-1	Gray	Major		P		P	P		P	Major	
4-2	Tan	Major		P		P	P		P		Minor
4-3	Gray	Major				P	P			Major	
4-4	Red	Minor	P	P		P	Major				
4-5	Tan	Major		P		P	P			Major	Minor
4-6	Gray	Major	P		P	P	P		P		Minor
4-7	Gray	Major	P	P	P	P	P			Major	Minor
11-1	Gray	Major	P	P	P	P	P			Major	Minor
11-2	Gray	Major	P	P	P	P	P	P		Major	Minor

Table 6. (cont.)



Color	Illite	Chlorite	M/C	C/M	Montmor-Illite	Montmor-Illonite	Montmor-Chlorite	Super-lattice Montmor-Mont-Ill	Montmor-illonite	Calcite	Quartz
Gray	Major		P		P	P				Major	Minor
Gray	Major	P	P		P	P					Minor
Tan	Major	P	P	P	P	P				Major	Minor
Green	Major	P		P	P	P		P		Minor	
Red	Major	P		P	P	P		P		Major	Minor
Red	Major	P		P	P	P				Major	
Red	Major	P		P	P	P					
Buff	Major	P		P	P	P				Major	
Green	Major	P		P	P	P					
Tan	Major	P		P	P	P				Major	Minor
Black	Major	P		P	P	P					Minor
Green	Major	P		P	P	P		P			
White	Major		P		P	P				Major	

Table 6. (concl.)



Color	Illite	Chlorite	Montmor-Chlorite M/C	Montmor-Chlorite C/M	Montmor-Illite	Montmor-Illite	Super-lattice Mont-Ill	Montmor-illonite	Calcite	Quartz
Gray	Major	P	P		P	P				Minor
Gray	Major	P	P	P	P	P	P		Major	
Brown	Major	P		P	P	P	P		Major	
Brown	Minor	P		P	P	Major	P			Minor
Tan	Major			P	P	P	P		Major	Minor
Tan	Major			P	P	P			Major	Minor
Black	Major	P		P	P	P	P			Minor

SCALE 2"=20', Eskridge Shale through the Long Creek Limestone.

LEGEND

Limestone

Cherty Limestone

Shale

Table 6 shows the lithologic relationship of the formations and members to the color, clay mineral content, quartz and calcite. It is possible by use of this table to see the montmorillonite chert relationship. The clay mineral relationship and description from the Florence Ls. through the Cottonwood Ls. was taken from McPherron (1956), with the exception of Blue Rapids Sh. which was analyzed in this investigation. Quartz and calcite shown in Table 6 are the non-clay minerals in the clay-mineral size fraction. The amounts indicated in these columns show the relationship between these non-clay minerals and the clay minerals in the clay-size fraction.

SUMMARY

The non-carbonate mineralogy of the limestones was determined by a petrographic mineral analysis and binocular microscope study. The binocular microscope was used on the insoluble coarse residue, greater than 125 microns in size. The major constituents of the coarse residue were chalcedony, muscovite, organic residue, and detrital quartz; and the minor constituents were chalcedonic fossil fragments, pyrite, magnetite, and limonite coated grains. The petrographic studies of the -125 micron to +53 micron fraction indicated chalcedony, limonite stained grains, pyrite, muscovite, celestite, and hematite coated grains to be the major constituents. Limonite staining was found on chalcedony and pyrite grains, but it could not be determined what grains were hematite stained. The minor constituents were found to be orthoclase, plagioclase, quartz, microcline, volcanic ash, tourmaline, rutile, hornblend, zircon, chlorite, and garnet.

The petrographic studies established the presence of hematite and limonite stained grains. These stained grains seemed to be related to the presence of pyrite, FeS_2, which was always present in large amounts in the samples that showed stained grains. The limonite and hematite seemed to be higher in samples that were exposed to surface weathering. In samples such as those of the Neva, which were collected from a fresh road-cut and also from an old road-cut, it was possible to determine a gradation from pyrite to limonite to hematite. The hematite indicating the most weathering, and the limonite less weathering. Therefore, a great deal of importance must be attached to the stage of surface weathering as well as sub-surface weathering.

The volcanic ash content in all samples was very low and ash was completely absent in most cases. The only samples which showed any ash in mentionable

quantity were from the Neva. The Neva also showed some free montmorillonite. Further studies should be made on the heavy and light fractions of all the shales and on both weathered and unweathered samples of the limestones and shales to clarify the problem of ash, chert and montmorillonite relationships.

In the petrographic and binocular studies care should be taken to start with as large a sample, before leaching, as possible. Samples should also be ground as fine as possible to insure complete carbonate removal and to speed up the removal of these carbonates. The heavy minerals were found in such small amounts that it was impossible to make a complete quantitative determination.

There seemed to be some relation between the iron and the chlorite found in the samples. Most of the chlorite found in the samples was believed to be the iron rich variety, which was present in both weathered and unweathered samples but in the fresh samples in very minor amounts. There was also a shortage of limonite and hematite in these fresh samples, but no lack of pyrite was noticed. It is the author's opinion, therefore, that a large per cent of the iron rich chlorites found in this area are due to the weathering of the pyrite within the formations.

The X-ray diffraction patterns failed to show any vermiculite in the samples. This may be explained by vermiculite being similar to montmorillonite or grading into montmorillonite and acting the same as montmorillonite when treated. G. F. Walker states in the "Clay Minerals Bulletin", August, 1957, page 162,

> "The fundamental similarity of smectites (montmorillonites) and vermiculites is such that the question naturally arises as to whether a distinction should be made at all, or whether the limits of the smectite (montmorillonite) group should be extended to include all swelling triphormic clay minerals and the name "vermiculite" be reserved exclusively for the macroscopic minerals. The question of treating vermiculites as

> smectites (montmorillonites) has already been raised (e.g., Roy and Romo 1954, Weaver 1956), but the incomplete nature of the evidence makes it appear inadvisable at this stage to attempt to reach final conclusions."

When the samples were treated with NH_4Cl and heated no collapse of the peaks could be noticed. These peaks also still expanded when glycolated, therefore, indicating montmorillonite rather than vermiculite as indicated in McPherron's (1956) work.

A random interlayered montmorillonite-chlorite-illite was noted in all samples. Samples were treated with HCl and heated. These samples were then glycolated and still expanded. Showing the presence of an expanding lattice mineral and the presence of chlorite was shown by the noticeable decrease in the peak size. These same samples were then treated with NH_4Cl and no noticeable movement or change in size of the peak could be noted; also, the peaks still expanded when glycolated. The samples were then heated to 450 degrees. This produced collapse of the 6.2A peak, but upon glycolation this peak expanded. If the expanding lattice mineral had been vermiculite it would not have expanded. The same results were noticed on the 7.2A peak. It was for these reasons the very prominent 6.2A peak was called a random interlayering of montmorillonite-chlorite-illite.

A super-lattice clay mineral was noticed in a great many of the samples, but all samples of the Johnson shale showed this clay mineral. These clays are composed of more than one clay mineral stacked so as to give measurements of the whole stack. These clays were encountered at such a high angstrom reading that it was difficult to make any definite mineral identification due to the approach to the main X-ray beam. As far as possible it was determined that the stacks were made up of two illite layers and one montmorillonite layer.

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CLAY MINERALOGY OF SOME PERMIAN SHALES AND LIMESTONES

by

LORIS ELDEN ASMUSSEN

B. S., Kansas State College
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AN ABSTRACT OF THE THESIS

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The purpose of the investigation was the determination of the clay and non-clay mineralogy of some of the Permian shales and limestones in the Manhattan area. An attempt was then made to correlate the presence of montmorillonite, volcanic ash, and chert. This investigation was conducted by the use of X-ray diffraction, petrographic mineral analysis, binocular microscope study, stain tests, and differential thermal analysis.

Samples collected were from the Council Grove Group of Permian age. They were the Blue Rapids Shale, Eskridge Shale, Neva Limestone, Bennett Shale, Glenrock Limestone, and Johnson Shale. They were collected by the spot type sampling method.

Charts were made of the limestones and shales to show the stratigraphic column, sample locations, color relationships, clay minerals, insoluble light minerals, insoluble heavy minerals, insoluble coarse residue, and X-ray diffraction patterns.

The following observations were made in connection with this investigation:

(1) A high pyrite, limonite, hematite content was noticed in the limestone samples. These three minerals seemed to represent three stages of weathering with the hematite being formed by weathering of limonite, and limonite by weathering of pyrite.

(2) It seems probable, both in the limestones and shales, that pyrite furnished the iron necessary for the formation of any iron rich chlorite present by a weathering process.

(3) Free montmorillonite was noticed in the unweathered samples of Neva as well as volcanic ash.

(4) Vermiculite seemed to be absent in most cases if not completely absent in all cases. The peak that was present at 7.2A was identified as

interlayer montmorillonite-chlorite and chlorite, with the chlorite being the degraded iron rich variety.

(5) A super-lattice clay was noted in several shales. There did not seem to be any of the super-lattice clays in the limestones studied. This may have been due to the carbonates masking the peak, or it may be that they do not occur in the limestone samples examined. The super-lattice clay probably represents a weathering stage since it was found only in more or less weathered samples.

(6) McPherron (1956) thought that there was a reciprocal relationship between the clay size quartz and the chlorite present in the shales he examined. In this investigation no relationship between clay size quartz and chlorite was found in the limestones examined, and in the shales the evidence was not conclusive.

(7) The clay minerals found in this investigation were chlorite, montmorillonite-chlorite, chlorite-montmorillonite, montmorillonite-chlorite-illite, montmorillonite-illite, illite, montmorillonite, and a super-lattice clay.